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NOVEL INHIBITION CHEMISTRY FOR OILFIELD SCALE MANAGEMENT

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A Thesis Submitted to the University of Huddersfield in Partial Fulfilment of the Requirement for the
Degree of Doctor of Philosophy

University of Huddersfield

School of Applied Sciences

2014

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ABSTRACT

The body of work presented here is focussed on five published papers which address solving inorganic scale problems experienced by the North Sea oil industry with a focus on the Norwegian Continental Shelf (NCS) over the last ten years or so. The degree of increasing difficulty in addressing issues of serious barium sulphate scaling, in the reservoir and wellbore areas, complicated by seawater breakthrough, the authorities demand for improvement in environmental properties of the chemistries deployed, the cost driven push for longer treatment life and with the increasing awareness of the damaging effects of deploying water based scale inhibitors into water sensitive reservoirs, is described in detail.

The work focuses on industry developed laboratory test methods, synthesising novel chemistries and developing improved deployment designs as a means of solving these significant problems.

The work is not a pure chemistry programme, it is an applied chemistry study focused on solving real-life oilfield scale problems. The project(s), planning and strategy involved leveraging knowledge and input from across the disciplines of production chemistry, petroleum engineering and near wellbore region modelling. It should be noted the real driver for the work was the inability of the available commercialised chemistries to resolve the problems. The resultant loss of production and associated remedial treatments were of a significant financial and environmental cost to the industry.

The papers cover the design testing and deployment of co-polymers and terpolymers to produce innovative molecules which offer higher performance scale inhibition and life of treatments in actively producing oil wells. The new molecules meet the environmental requirements of biodegradation, bioaccumulation and toxicity.

The projects offered are under the following headings:

- Enhanced inhibitor squeeze treatment life through "Bridging"
- Field experiences in Application of Inhibitor Interactive Packages Resulting in Increased Squeeze Life.
- Development of multi-functional chemicals for efficient "fines" control and squeeze life enhancement in producing oil wells.

- Development of highly efficient and environmentally friendly scale inhibitor molecules for oilfield use, including reference to more efficient placement technology.
- Oil soluble scale inhibitor development.

The papers describe synthesis, laboratory testing and field deployment experiments leading to adoption of the new technology by multi-national oil companies. In most cases patents have also been granted. The value added of the work is also quantified in both environmental and financial aspects.

ACKNOWLEDGEMENTS

I would like to acknowledge the considerable support and encouragement I have received from colleagues I have had the fortune to work with on the subject of Oilfield Scale. In particular from my time with Exxon Chemical, Champion Technologies ,Statoil and Heriot Watt University. Indeed it was Professor K.S. Sorbie who suggested many years ago I should approach this project via the published papers route. When I had the time available to focus on this thesis and do the subject justice it actually was a pleasure to put the effort in. I would encourage anyone with similar aspirations to "just get started"

I draw reference to the particular inspiration I received from the author discussion and subject matter within the published theses of Prof E.J. Mackay, Dr Gordon Graham, Dr Ping Chen, Dr Tao Chen together with the detailed research projects jointly undertaken with the Statoil team.

I am indebted to my joint authors of the selected published papers and of the support papers referenced within this work.

I have been greatly helped by the guidance and enthusiasm provided by my supervisors Professor D.R. Brown and Dr N.T. Powles of Huddersfield University. Without them this project could not have been undertaken.

GLOSSARY

Permeability	<p>The ability or measurement of a rock's ability to transmit fluids typically measured in darcies or millidarcies.</p> <p>Sandstones which are permeable and transmit fluids easily tend to have many large well connected pores.</p>
Relative permeability	<p>Is the ratio of effective permeability of a particular fluid at a particular saturation to the absolute permeability of that fluid at total saturation</p>
Porosity	<p>The capacity of the rock to hold liquids in the pores, ie total pore volume per unit volume of rock – is measured in volume/volume percent or porosity units.</p>
Productivity index (PI)	<p>Calculated from dividing pressure drop over tubing into the flowrate of oil</p> <p>Units $\text{Sm}^3/\text{day}/\text{bar}$ (which Sm^3 is standard m^3). It is a mathematical way of expressing the ability of a reservoir to deliver fluids to the wellbore. Alternatively the PI is usually stated as the volume delivered per psi of drawdown at the sand face (perforations) in $\text{bbls}/\text{day}/\text{psi}$.</p>
Pore	<p>Is a discrete void within a rock which can contain air, water, hydrocarbons or other fluids. In a body of rock the percentage of pore space is the porosity.</p>
Pore volume (PV)	<p>The total volume of the pores in a core plug. Each total sweep of liquid of that volume is referred to as 1 pore volume.</p>
Squeeze	<p>Displacement of fluids in reverse flow down the tubing and out into the reservoir. Normally to carry chemicals to the near wellbore area of the reservoir.</p>
Water clean up/oily water	<p>Refers to the initial back produced fluids water component after a squeeze.</p> <p>The amount of oil in the water and its degree of dispersion can be difficult to handle in the production system causing high ppm of oil in the water giving unacceptable water quality. Target is <40 ppm (parts per million).</p>

Perforations	The holes punched in the casing allowing fluids to be produced into the tubing from the reservoir.
Perforated interval	The height of perforations usually in feet.
HTHP	High Temperature High Pressure. Usually refers to conditions in the reservoir and the fluids entering the tubing. Normally deeper wells are higher temperatures. The gas ratio can give higher pressure reservoir. Normally temperature over 120°C and pressures over 200 bar are referred to as HPHT.
Formation water (FM)	The water composition in the reservoir usually within the pores.
SW	Sea water. Commonly utilised to maintain reservoir pressure. The seawater is pumped, at high pressure down special prepared injection wells to the reservoir.
SR	<p>Saturation Ration refers to how much salts are dissolved in a brine under certain conditions of temperature and pressure. If SR is >1 the solution is supersaturated. If SR =1 the solution is in equilibrium with the precipitating phase.</p> <p>SR is calculated from the 'ionpairing' Pitzer equation.</p> $SR = \ln ([Me] [An] / KSp)$ <p style="margin-left: 40px;">KSp = solubility product of the scales MeAn</p> <p style="margin-left: 40px;">[Me] = concentration of cation</p> <p style="margin-left: 40px;">[An] = concentration of anion</p>
SI	<p>Saturation Index.</p> $SI = \log_{10} ([Me] [An] / KSp)$
BS&W	Base Sediment and Water. Refers to the amount of water in the oil production together with any solids (sediment) which can be sand, for example. Expressed at a percentage of the total fluids.

SWB	Sea Water Breakthrough. Refers to the amount of seawater, from seawater pressure maintenance injection, which is now arriving at the tubing having swept across the reservoir from its point of injections.
Threshold Concentration/MIC	Refers to the ppm (parts per million) of scale inhibitor needed to stop scale precipitating.
ESP	Electric Submersible Pumps. Usually placed down a low pressure well to aid lifting the oil to the surface.
Fines	Small particles of clay(s). Normally from loosely consolidated reservoirs. Sand can also be produced at same time.
Gel package	Packages which raise the viscosity of a liquid being deployed down a well of long distance and multi-perforated zones. Particularly horizontal wells. The change in rheology gives better distribution along the length of the well producing zones.
Water block	A condition where the near wellbore zone becomes water saturated and has its wettability changed to 'water wet' . This changes the permeability to oil and blocks the flow of oil. Can also be due to swelled clay particles blocking the pores causing reduction in permeability.
Coning	When produced formation water is sucked into a producing well. Usually occurs in gas wells which are being produced at high rates. The water ingress is at the expense of oil or gas production and will further exacerbate the issue by water wetting the rock and changing the rel perm (relative permeability) to oil resulting in lost production.
BHMT	Bis hexamethylene pentakis methylene phosphonic acid. Phosphonate type scale inhibitor.
DETA	Diethylene triamine tetra methylene phosphonic acid. Phosphonate type scale inhibitor.

PRINCIPAL THESIS PUBLICATIONS (INCLUDED IN APPENDIX I)

PAPER 1 A Way Beyond Scale Inhibitors – Extending Scale Inhibitor Squeeze Life Through Bridging (SPE 80377) PCT/GB2007/003131

O.M. Selle, Montgomerie et al. Paper contribution 50%.

This paper was prepared for presentation at the 2003 SPE International Oilfield Scale Conference held in Aberdeen, UK, 30-31 January 2003.

The paper was further published by Journal of World Oil.

PAPER 2 Field Experiences in the Application of an Inhibitor Interaction Package to Extend an Inhibitor Squeeze Life (SPE 100466) PCT/GB2006/002877

Chen, Montgomerie et al. Paper contribution 70%.

This paper was prepared for presentation at the 2006 SPE International Oilfield Scale Conference held in Aberdeen, UK, 1 June 2006.

The paper was further refereed, translated into Chinese and published in China by Journal of Foreign Oilfield Engineering, Volume 24, Number 4, 2008 (Professor S Ren) (see Appendix I)

PAPER 3 Development of a New Co-polymer Inhibitor Chemistry for Downhole Squeeze Applications (SPE 113926) PCT/GB2006/002877

Montgomerie et al. Paper contribution 85%.

This paper was prepared for presentation at the 2008 SPE International Oilfield Scale Conference held in Aberdeen, UK, 28–29 May 2008.

The paper was further refereed and published by SPE Production & Operations; Volume 24, Number 3 August 2009.

**PAPER 4 Meeting the Challenges in Downhole Scale Control for High Water Production
Horizontal Wells in Environmental Sensitive Part of Norway North Sea. A New
Terpolymer is Developed, (SPE 135249) PCT/GB2007/000099**

Chen, Montgomerie et al. Paper contribution 80%.

The paper SPE 135249, published by SPE and presented in SPE Annual Conference, Florence November 2010, has now been peer reviewed and further published by the Journal of SPE Production & Operations 2012.

PAPER 5 Oil Soluble Scale Inhibitor (SPE 50706) US Patent 6,379,612, 30 April 2002

Montgomerie et al. Paper contribution 75%.

This paper was prepared for presentation at the 1999 SPE International Oilfield Scale Conference held in Aberdeen, UK, January 1999.

The paper was further published by SPE Journal of Petroleum Technologies, March 1999.

ADDITIONAL CO-AUTHORISED PUBLISHED PAPERS

SPE Papers

1. "The Development of Corrosion Inhibitors with Low Environmental Toxicity" paper SPE 24846 presented at the 6th SPE Annual Technical Conference and Exhibition of the Society of Petroleum Engineers held in Washington DC, October 4-7, 1992.
2. "Development of Oil Soluble Scale Inhibitor", SPE paper presented at the 1999 First International Symposium on Oilfield Scale., held in Aberdeen, UK, January 1999.
3. "The Applications of Oil Soluble Inhibitors into Texaco Galley Reservoir. A Comparison with Traditional Squeeze Technique to Avoid Problems Associated with Wettability Modifications in Low Water-Cut Wells", paper SPE 60197 presented in the Fifth International Symposium on Oilfield Scale held in 25-27 January. 2000, Aberdeen.
4. "Understanding the Mechanisms of Halite Inhibition and Evaluation of Halite Scale Inhibitor by Static and Dynamic Tests", paper SPE 121458 to be presented at the 2009 SPE International Symposium on Oilfield Chemistry to be held in The Woodlands, Texas, 20-22 April 2009.
5. "Development of Environmental Friendly Iron Sulphide Inhibitors and Field Application", paper SPE 121456 to be presented at the 2009 SPE International Symposium on Oilfield Chemistry in The Woodlands, Texas.
6. "Development of Test Method and Inhibitors for Lead Sulfide", SPE 130926, paper presented at SPE 10th International Symposium on Oilfield Scale, Aberdeen, May 2010.
7. "Development of Non-Aqueous/Low Density Scale Inhibitor Package for Down-hole Squeeze Treatments", SPE 130686, paper presented at SPE 10th International Symposium on Oilfield Scale, Aberdeen, May 2010.
8. "Modelling a Series of Non-Aqueous Field Scale Inhibitor Squeeze Treatments in the Heidrun field", SPE 131496, paper presented at SPE 10th International Symposium on Oilfield Scale, Aberdeen, May 2010.
9. "Meeting the Challenges in the Downhole Scale Control for High-Water-Production Horizontal Wells in Environmentally Sensitive Part of the Norwegian North Sea", paper SPE 135249, presented at the 2010 SPE Annual Technical Conference and Exhibition (ATCE), 19-22 September 2010 in Florence, Italy.
10. Modelling a Series of Non-Aqueous Field Scale Inhibitor Squeeze Treatments in the Heidrun field", SPE 131496, paper published in SPE Journal Production & Operations April 2011.

11. "Novel Scale Squeeze Technology and Treatment Designs for Improving Scale Inhibitor Retention and Treatment Lifetimes - Use of Ionic Polymers in the Overflush". SPE 154935 presented at SPE 1st International Symposium on Oilfield Scale, Aberdeen, May 2012.
12. "Understanding the Co-deposition of Calcium Sulphate and Barium Sulphate and Developing Environmentally Acceptable Scale Inhibitors Applied in HTHP wells SPE 156013 presented at SPE 11th International Symposium on Oilfield Scale, Aberdeen, May 2012.
13. "Development of Test Method and Environmentally Acceptable Inhibitors for Zinc Sulfide Deposited in Oil and Gas Fields". SPE 156005 presented at SPE 11th International Symposium on Oilfield Scale, Aberdeen, May 2012.
14. "Understanding Mechanisms of Scale Inhibition Using Newly Developed Test Method and Developing Synergistic Combined Scale Inhibitors". SPE 156008 presented at SPE 11th International Symposium on Oilfield Scale, Aberdeen, May 2012.
15. "Development of an Environmentally Friendly Polymer Scale Inhibitor for Tight Carbonate Reservoir Squeeze Treatment". OTC 23352 Paper presented for the 2012 Offshore Technology Conference to be held in Houston, TX.
16. "New Environmentally Acceptable Chemistry and Evaluation Methods for Scale Inhibitor Testing Under Turbulent Flow and Harsh Scaling Conditions". SPE 155428 presented at SPE 11th International Symposium on Oilfield Scale, Aberdeen, May 2012.
17. "New Polymer Chemistry for Squeeze Application in Tight Carbonate Reservoirs". SPE 154953 presented at SPE 11th International Symposium on Oilfield Scale, Aberdeen, May 2012.
18. "Meeting the Challenges in the Downhole Scale Control for High-Water-Production Horizontal Wells in Environmentally Sensitive Part of the Norwegian North Sea", paper published in SPE Journal Production & Operations October 2012.
19. "Scale Squeeze Treatments in Short Perforation and High Water Production ESP Wells - Application of Oilfield Scale Management Toolbox", The 6th International Petroleum Technology Conference (IPTC), 26-28 March 2013 in Beijing, China.
20. "Study of Sand like Scale in the Bottom Hole", SPE paper presented at SPE 12th International Symposium on Oilfield Scale, Aberdeen, May 2014.
21. "Development of Novel Test Methodology to Understand the Mechanisms of Halite Inhibition and Environmentally Acceptable Halite Scale Inhibitors for HPHT Application". SPE paper 169803 presented at SPE 12th International Symposium on Oilfield Scale, Aberdeen, May 2014.

22. "Influence of Calcium and Bicarbonate Ions on the Kinetics of CaCO₃ Formation at HTHP in the Absence and Presence of Scale Inhibitors". SPE paper presented at SPE 12th International Symposium on Oilfield Scale, Aberdeen, May 2014. SPE 169769
23. "Do We Need Higher Dose Scale Inhibitors to Inhibit Scale under Turbulent Conditions? Insight into Mechanisms and New Test Methodology". SPE paper presented at SPE 12th International Symposium on Oilfield Scale, Aberdeen, May 2014. SPE 169780
24. "The True Impact of Pre-flush Additives on Scale Squeeze Treatments - Application of Modelling and New Test Methodologies to Understand Mechanisms of Retention and Optimise Field Treatment Designs". SPE paper presented at SPE 12th International Symposium on Oilfield Scale, Aberdeen, May 2014.
25. "Mechanisms, New Test Methodology and Environmentally Acceptable Inhibitors for Co-deposition of Zinc Sulfide and Calcium Carbonate Scales for HTHP Application". SPE paper 169810 presented at SPE 12th International Symposium on Oilfield Scale, Aberdeen, May 2014.

Geilo Papers

26. "Squeeze Application Using a Polymer Inhibitor – A Case History", Paper presented in the 4th Norwegian International Oilfield Chemical Symposium, 18 – 21 April 1993. Geilo, Norway.
27. "Scale Inhibitor Squeeze Treatments – Validity of Laboratory Core Tests", Paper presented in the 6th Norwegian International Oilfield Chemical Symposium, 19 – 22 March 1995. Geilo, Norway.
28. "Application of Oil Soluble Inhibitors", Paper presented in the 9th Norwegian International Oilfield Chemical Symposium, 22 – 25 March 1998. Geilo, Norway.
29. "A Scale Inhibitor Chemistry Developed for Downhole Squeeze Treatments in a Water Sensitive and HTHP Reservoir", paper to be presented in the 19th Norwegian International Oilfield Chemical Symposium, March 2008. Geilo, Norway.
30. "Development of Halite Test Methodology, Inhibitors and Field Application", paper to be presented in the 20th Norwegian International Oilfield Chemical Symposium, March 2009. Geilo, Norway.
31. "Field Experiences in the Application of an Improved Yellow Scale Inhibitor in an Environmentally Sensitive Field", paper presented in the 21st Norwegian International Oilfield Chemical Symposium, 15-17 March 2010. Geilo, Norway

32. "Development of Environmentally Acceptable, Non Corrosive, Iron Sulfide Scale Inhibitors for Gas Lift Application", paper presented in the 22nd Norwegian International Oilfield Chemical Symposium, March 2011. Geilo, Norway.
33. "Preflush and/or Overflush Ionic Polymer Additives in Scale Squeeze Treatments - Application of New Test Methodologies to Understand Mechanisms of Retention and Optimize Field Treatment Designs", paper presented at the 25th International Oil Field Chemistry Symposium, on 23- 26 March 2014. Geilo, Norway.
34. "Further Insights into Mechanisms of BaSO₄ Control under Turbulent Conditions and Development of Environmentally Acceptable Squeeze Inhibitors", paper presented at the 25th International Oil Field Chemistry Symposium, on 23- 26 March 2014. Geilo, Norway.

NACE Papers

35. "Environmentally Friendly Corrosion Inhibitors for CO₂ Corrosion for North Sea Oil Fields", NACE Corrosion 2000, Paper 20.
36. "Development of Low Corrosive Environmental Friendly Calcium Carbonate Scale Dissolver for HTHP Wells", paper presented in NACE 2010.
37. "Development of Environmentally Friendly Calcium Carbonate Scale Inhibitor for HTHP Squeeze Application in the Oil and Gas Field Water Treatment", NACE 2011, March 13-17, 2011. Houston, Texas
38. "Development of an Environmentally Friendly Polymer Inhibitor for Short Perforation and High Water Production ESP Wells", Paper C2013-0002661, CORROSION 2013, March 17-21, 2013. Orlando, Florida, USA.
39. "Development of Test Methods and Inhibitors for Halite Deposition in Oilfield Water Treatment", Paper C2013-0002659, CORROSION 2013, March 17-21, 2013. Orlando, Florida, USA.

PATENTS GRANTED LIST

Patent Number	Application Number	Patent Name	Inventor
Australia 2006274668	PCT/GB2006/002877	SI Co-polymer	Montgomerie, et al
Europe 1910495	PCT/GB2006/002877	SI Co-polymer	Montgomerie, et al
Canada 2614868	PCT/GB2006/002877	SI Co-polymer	Montgomerie, et al
US 8586511	PCT/GB2006/002877	SI Co-polymer	Montgomerie, et al
Australia 2008263581	PCT/GB2008/050432	Foam well treatment	Selle, Montgomerie, et al
Europe EP2173831 B1	PCT/GB2008/050432	Foam well treatment	Selle, Montgomerie, et al
US 8653008	PCT/GB2008/050432	Foam well treatment	Selle, Montgomerie, et al
Canada 26901784	PCT/GB2008/050432	Foam well treatment	Selle, Montgomerie, et al
Australia 2007207243	PCT/GB2007/000099	SI Terpolymer	Montgomerie, et al
Europe EP1981947	PCT/GB2007/000099	SI Terpolymer	Montgomerie, et al
Canada 2635032	PCT/GB2007/000099	SI Terpolymer	Montgomerie, et al
US 8343897	PCT/GB2007/000099	SI Terpolymer	Montgomerie, et al
Canada 2660097	PCT/GB2007/003131	SLE	Montgomerie, et al
Australia 2007285556	PCT/GB2007/003131	SLE	Montgomerie, et al
Europe EP2052050	PCT/GB2007/003131	SLE	Montgomerie, et al
US 8101554	PCT/GB2007/003131	SLE	Montgomerie, et al
		SLE – Additive in the post flush	
US Patent 6,379,612	30 April 2002	Oil Soluble/inhibitors Scale	Reiser, Montgomerie, et al

CHAPTER 1
INTRODUCTION
CHAPTER 1 INTRODUCTION

1. INTRODUCTION

Oilfield scale is the "Cardiovascular Disease" of oil production and is generally thought of comprising the inorganic salts such as the carbonates and sulphates of the Alkaline Earth metals calcium, strontium and barium. Scale may also manifest itself as complex salts of iron such as sulphides, hydrous oxides and carbonates.

Scaling is normally related to precipitation. However, precipitation does not always lead to scaling.

The deposition of mineral scales depends on a number of variables including^{1,54,63}:

- degree of saturation of water
- rate of temperature change
- degree of agitation during formation of crystals
- size and number of seed crystals
- presence of impurities
- change in pH of solution^{42,43}
- changes in system pressure.

Oilfield scale forms in one of two ways. 1. First a brine (eg formation water) undergoes a change in conditions such as temperature or pressure. This generally gives rise to the carbonate scales or NaCl scale in HTHP (high temperature, high pressure) wells. Second, two incompatible waters (eg formation water rich in calcium, strontium and barium and sea water high in sulphate mix. This generally gives rise to sulphate scales^{12,15,60}.

Iron scales (sulphides when production is sour, hydrous oxides when production is sweet) usually reflect the corrosion in the system. The source of iron is predominantly the pipework and vessels in the system itself.

Analysis of typical formation waters for several North Sea fields and North Sea water are attached in the Appendix IV. The formation waters reflect the variation in formation water chemistry encountered in North Sea reservoirs.

Problems caused by Scale does not restrict itself to any particular location in the oilfield, although some locations are more important than others in terms of ease and cost of remedial or preventative treatment options.

The economic impact of these options on field development plans can be very significant, particularly in subsea environments, and can even make the difference between sanction and rejection of a

project. Typical chemical costs for scale squeezing an offshore production well would be in the range \$40,000 - \$150,000^{2,5,55}. If the treatment can be effectively deployed by pumping from the surface without specifically controlling the downhole injection profile (bullheading), then the chemical is the most significant component of the cost. However, if the treatment requires to be deployed via coiled tubing from a diving support vessel (DSV), then rig hire costs in the range \$100,000 - \$300,000 per day can easily dominate the treatment costs, with rig hire potentially being required for 3 - 5 days per treatment per well in shallow water (<400 m) environments, escalating in deepwater. Sulphate removal package costs may be in the range \$10 - \$40 million, depending on the volume of water to be treated daily.

However, the full CAPEX cost for sulphate removal must include deck loading costs, space constraints, and power consumption. OPEX costs of \$750,000 - \$1,000,000 per annum (for filter and membrane replacement, biocides and scale inhibitors) should also be included in the calculation, meaning that the total figure may require to be multiplied by a factor of 2.5 - 10, depending on the production processing infrastructure.

Hence it is evident that significant costs may be involved in scale management, particularly in subsea and deepwater environments, and accurate techniques for estimating potential CAPEX and OPEX costs are essential⁵⁵.

1.1 Drilling

Scale can cause problems during drilling and completion of a well if the drilling mud and/or completion fluid is incompatible with the formation water. For example, allowing a seawater based mud to contact a formation water rich in barium and strontium ions would be undesirable, as would allowing a high calcium brine to contact a formation water rich in bicarbonate.

Clearly, drilling the first well in a new prospect is potentially very hazardous and a more dense mud than actually required will probably be used, increasing the risk of invasion and formation damage due to scale. There is no way of knowing the chemistry of the formation water which will be met although estimates based on geological and geochemical correlations are feasible. The collection and analysis of representative water samples as soon as possible is obviously beneficial if the consequences of drilling mud filtrate invasion are to be assessed and allowed in future wells in the field.

1.2 Water Injection

Problems may arise at the commissioning stage of new injectors if the injection water is incompatible with the formation water. For example, seawater injection into an aquifer rich in strontium and/or barium ions can cause sulphate scale deposition. Problems from sulphate scale can be omitted by injecting aquifer water or by sulphate removal treatment of the injected seawater.

1.3 Reservoir Damage

The effect of scale precipitation deep in the reservoir is an aspect which appears not to have been seriously addressed by reservoir engineers. The question being: does scale precipitation in the reservoir impair or improve the recovery of oil? A suitable study should consider the implications of^{5,12,15,60}:

- injection of seawater into an aquifer
- movement of seawater through the residual oil zone
- movement of seawater through oil zone
- the effect of mixing of seawater and formation water within the reservoir
- consequences of ion-exchange and rock mineral dissolution processes on the bulk chemistry of the floodwater.

Intuitively, the effect of scale precipitation in the reservoir will be small⁵⁵. However, the consequences of effective scaling of specific zones can be significant.

Scale precipitation in the near wellbore area can be quite detrimental to the inflow properties and the productivity of the well. Most of the scale inhibitor squeeze treatments are performed in producing wells in order to prevent scaling in the near wellbore area and tubing.

1.4 Water Production

As soon as a production well begins to cut water (0.5 – 1 %), a risk of carbonate scale formation occurs. The severity of the problem depends on the water chemistry and is aggravated by high drawdowns when carbonate scale may be laid down in the actual formation. Under certain conditions formation water and injection (sea) water flow together towards the wellbore, laying down scale where they mix. When this mixing occurs in the near wellbore area, severe productivity reductions due to scaling may occur.

1.5 Production Operations

Once significant water production has occurred, process equipment such as heat exchanges, valves, pumps, filters and all associated pipework are at risk. Super-saturation may be caused by changing the temperature and pressure of a water, or by mixing incompatible waters. The latter possibility may arise from a process operation (sand-washing, desalting, jetting, etc) or because waters from different formations (comingled production or different wells) are mixed in the production system. The last point is particularly noteworthy; even if a well with seawater breakthrough has not suffered damage, the water which that well produces is unlikely to be compatible with formation water, and mixing such waters from different wells in the production system will sooner or later cause scaling problems. Scale deposits in the downhole safety valve will represent a safety risk, and scale deposits on downhole production tubing can be an obstacle to well interventions.

1.6 Radioactivity Associated with Sulphate Scale Deposition

Barium sulphate scale can easily deposit as a mixed scale containing strontium, calcium and radium. Radium, which is an alkaline earth metal with similar chemical properties to barium, often co-precipitates. In this way, naturally occurring radioactive materials (NORM) such as radium, may effectively be concentrated in the sulphate scale formation and deposition. This leads to radioactive scale and special precautions have to be taken regarding handling and disposal of such scales. Special regulations for handling and storage of NORM scale exist⁵⁶.

1.7 Scale Control Strategy

Once an understanding has been developed of the potential for scale precipitation in the reservoir and production system, the technique of applying reservoir simulation calculations may be used to study the impact of the various scale control strategies that might be employed. These range from controlling the composition of injected brines, to chemically inhibiting the scaling reaction, usually in and around the production wells. The design of scale inhibitor "squeeze" treatments in production wells may be influenced by subsurface fluid pressure and flow conditions, and it is possible to use reservoir simulation calculations to predict the impact of these flow conditions on the effectiveness of squeeze treatments^{2,3,55}.

1.8 Scale Formation

Oilfield scales are hard mineral compounds that precipitate from brine solutions⁶. The solids that form (Figures 1.1 and 1.2)^{4,55} may adhere to solid surfaces in the reservoir (Figure 1.3), or be transported as a suspension⁵⁵ (Figure 1.4) which can then plug sand screens (Figures 1.5 and 1.6) or stabilize oil-water emulsions, thus creating difficulties with separation. They may also adhere to solid surfaces in the subsurface production tubing (Figures 1.7 and 1.8) and other hardware such as electric submersible pumps (ESPs), surface flow lines (Figure 1.9) or separation equipment (Figures 1.10 and 1.11). The impact such constrictions would have on flow, and hence on productivity, is self-evident. Safety may be compromised by scale deposition in sub-surface safety valves (SSSVs), and some scales constitute a health hazard, as they are naturally occurring radioactive materials (NORM) that may be expensive and dangerous to remove and dispose of.

There are two principal types of scales: carbonates and sulphates. The two types form by completely different mechanisms, yet they manifest themselves in the same location. Unfortunately, this tends to be production wells and their immediate environs.

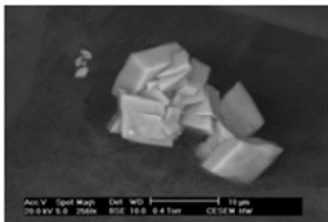


Figure 1.1 : BaSO₄ crystals

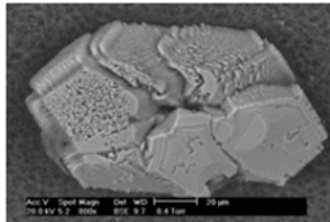


Figure 1.2 : CaCO₃ crystals



Figure 1.3 : BaSO₄ crystals plugging pore space



Figure 1.4 : Suspension



Figure 1.5 : Clean sand screen



Figure 1.6 : Plugged sand screen



Figure 1.7 : Scaled production tubing

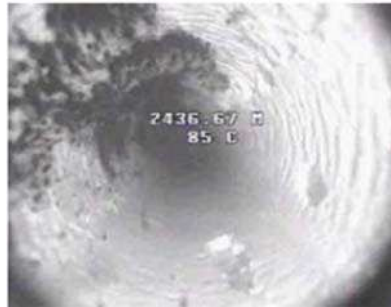


Figure 1.8 : Scaled production tubing. (Note gouges caused by video tool)



Figure1. 9 : Scaled surface flow line



Figure 1.10 : Scaled baffles in separator



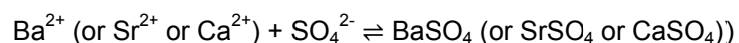
Figure 1.11 : Same baffles after cleaning

Figures 1.1 to 1.11 by kind permission of MacKay, E.J.⁵⁵.

Carbonate scale formation occurs when the pressure of produced connate water or aquifer water decreases below the bubble point and carbon dioxide is evolved. As carbon dioxide is evolved, the solubility with respect to carbonate declines rapidly and a precipitate forms with divalent ions such as iron, and more commonly calcium, as outlined in the following equation (Equation 1)



Where water injection (seawater, river, aquifer or produced water) is used for pressure maintenance and sweep, the mixing of incompatible brines can lead to the formation of sulphate scales should the injection water contain sulphate ions (Equation 2).



In a production operation where barium is present within the formation water and seawater is the injected fluid, the principal flow assurance risk is barium sulphate scale.

This is due to its very low solubility relative to calcium carbonate and sulphate scales of strontium and calcium.

1.9 Scale Prediction, Inhibitor Chemistry and Mechanisms, Management and Applications

1.9.1 Sulphates

The deposition of sulphate scale is closely related to sea water injection for pressure support in the reservoir. How sea water flows through the reservoir and into the production well is important for the potential sulphate scale problem in the producers.

Sulphate scale will normally form at the spot where sea water and incompatible formation water mix⁵⁴. If this mixing takes place deep into the reservoir the deposited scale is not expected to do much harm. It may even contribute to improved water sweep through the reservoir. On the other hand, if the mixing occurs in the reservoir near the wellbore, significant formation damage due to scaling can occur^{12,15,60}.

How the sea water breakthrough occurs may therefore be of some significance for the scaling situation in a producing well. Two different conditions may be considered:

1. Pure formation water is produced at water breakthrough. After seawater breakthrough, the seawater fraction in the produced water will increase slowly.
2. A significant amount of seawater (>10%) is mixed into the formation water at water breakthrough.

Normally condition 1 is expected to give the most severe scaling problems. Wells with water breakthrough similar to condition 1 are known to develop sulphate scaling problems in the near wellbore area.

Regarding condition 2 it is expected that most of the mixing of seawater and formation water and resultant scale deposition takes place deep in the reservoir. Most of the scale is precipitated before the mixed water reaches the producing well, and the scaling potential for this mixed water is therefore less when it arrives at the perforations. Normal scale prediction calculations do not consider the different mixing scenarios or deposition kinetics, and scale predictions are mainly based on thermodynamic equilibrium calculations.

An example of a scaling tendency calculation^{3,9,10,54}, is shown in Figures 1.12 and 1.13. The equilibrium amount of precipitates are shown as functions of % seawater in the produced seawater/formation brine mixture.

At composition ~10 % sea water a larger amount of barium sulphate will precipitate at a lower supersaturation. At composition ~50 % sea water less barium sulphate will precipitate but the supersaturation is higher (see Figure 1.13).

The higher super saturation at ~50 % sea water compared to 10% indicate a stronger thermodynamic driving force for precipitation of barium sulphate scale. Effective inhibition may be more difficult to obtain for the 50:50 FW-SW situation compared to the ~10% SW situation, and normally a higher inhibitor threshold concentration will be required.

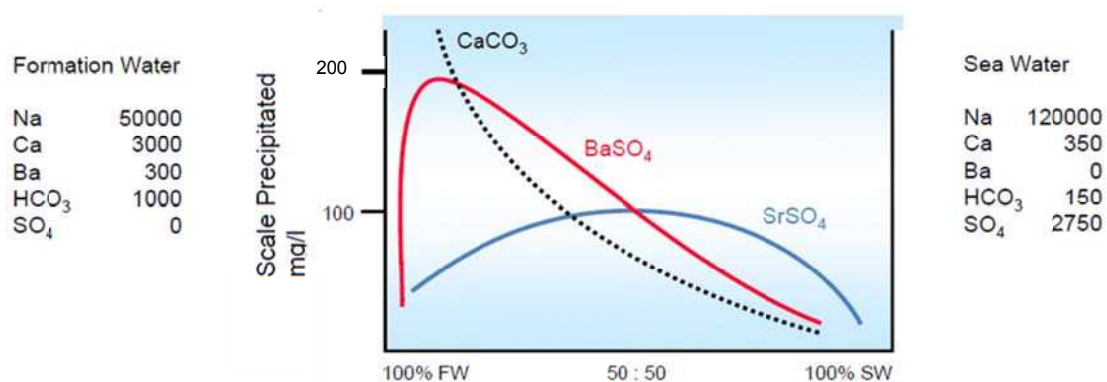


Figure 1.12 : Predicted scale precipitation upon mixing of formation water and sea water^{54,57,58}

As seawater breakthrough increases the severity of scaling reaches a peak and then declines. This likely means a need to change inhibitor dosage to reflect changing scaling tendency.

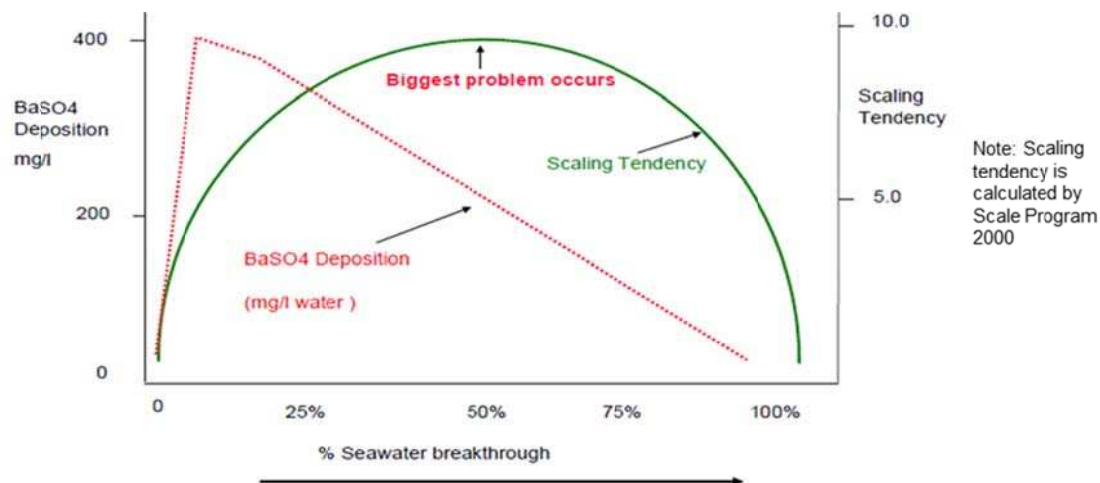


Figure 1.13 : Calculated amount of BaSO_4 and scaling potential upon mixing of Formation water and sea water⁵⁴

As can be seen barium sulphate precipitates most around 90:10 FW:SW. The precipitation continues to 50:50 ratio when the amount starts to drop off. However the scale tendency shows the thermodynamic driving force at 50:50 is stronger.

1.9.2 Carbonates

Reliable prediction of carbonate scale⁶¹ is more difficult than that of sulphate scale since it requires accurate data on downhole pH, downhole saturation of CO_2 and downhole concentration of HCO_3^- .

These data are not independent and the accuracy of the data can often be questionable⁶². In the calculations it is assumed that the formation water is saturated with respect to calcium carbonate at initial reservoir conditions. This assumption is used in calculating the downhole concentration of bicarbonate, pH and the downhole saturation of CO_2 from laboratory measured ion concentrations of the brine where the measurements are made on brine samples at ambient conditions.

The MultiMEGSCALE model is used for these calculations. The PVT reference model calculates the carbon dioxide partitioning between gas, oil and water. Figure 1.14 shows the isosaturation curves for calcium carbonate in a well.

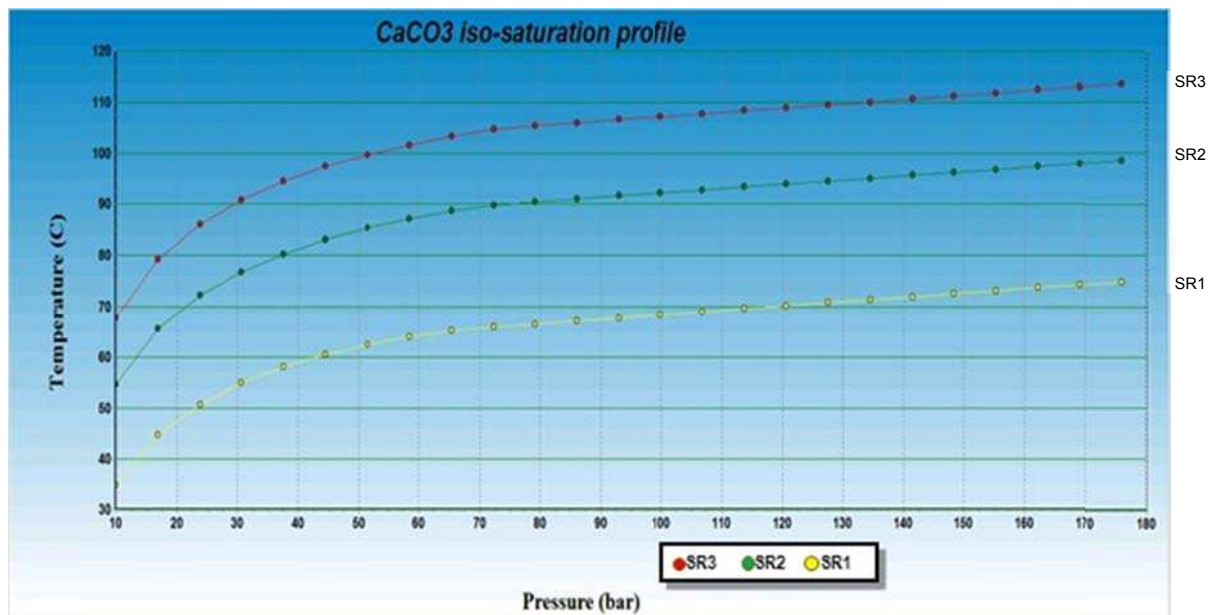


Figure 1.14^{54,57,58} : Isosaturation curves for CaCO_3 for a NCS formation water, illustrating the scaling potential

SR in the saturation ratio calculated^{57,58} by the scale prediction program, eg Scale 2000. The SR is calculated for the Temperature and Pressure of the system being studied.

If $\text{SR} < 1$ the solution is under saturated

$\text{SR} = 1$ the solution is in equilibrium with the precipitating phase

$\text{SR} > 1$ the solution is supersaturated.

As shown above the solution supersaturates and precipitates scale at increasing temperature and pressures with lowering SR values.

Carbonate scaling calculations are sensitive to pH and accurate determination of alkalinity in the water is important for a reliable carbonate prediction.

The pH in the water sample should be measured^{57,58,59,61} on the platform/rig immediately after sampling. Storing of the sample will cause the pH of the water to change. The amount of organic acids dissolved in the brine influence the pH and the alkalinity of the brine. The organic acid content needs measured.

The scaling situation will normally change during the field's lifetime. The potential for carbonate scale is normally highest at early water breakthrough and low water cut while the sulphate scale potential is highest at about 50:50 mixing of formation water and sea water. However, due to the dilution effect^{12,15,60} the potential amount of BaSO_4 to precipitate is highest at low sea water cut. This means that the potential damage from BaSO_4 scale precipitation is highest at low sea water cut. Figure 1.15

illustrates the change in scaling potential versus time for a typical field having sea water injection for pressure support.

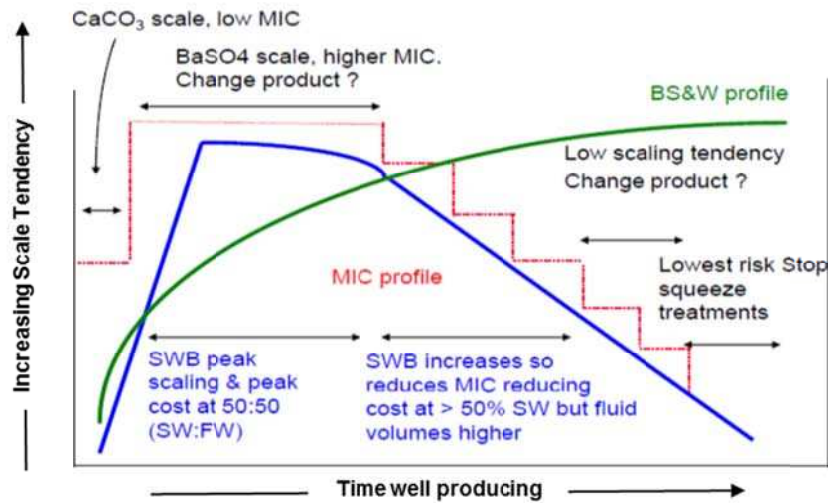


Figure 1.15 : Figure to illustrate the change in scaling potential vs. time for a typical field with sea water injection for pressure support⁵⁴

1.9.3 Scale Potential and Predictive Models

Scale formation in oilfield brines takes place in a multicomponent, multiphase environment. The first step in determining if there will be a scaling problem for a particular reservoir, is to carry out a scale prediction calculation^{9,60}. Several computer models are available for scale prediction, and a recommended models to use are MultiMEGSCALE (2). (Multiscale) used in Norway and Scale Soft Pizer from Rice University, USA.

Scale prediction and modelling is not the focus of this thesis. The inclusion is only to give an understanding of the scale process and the tools available to the industry to understand and plan scale control strategy.

Numerous 'models' and industry papers detailing the calculations and accuracy of the models are available viz eg SPE 68302⁷ and SPE 132237⁸.

1.9.4 Life Cycle Management of Scale Control

Flow assurance is an essential aspect of the economic production of crude oil. It may be defined as the ability to produce petroleum fluids economically from the reservoir to a production facility over the lifetime of a field.. Therefore, scale control needs to be addressed as part of asset life cycle

management. Such an approach allows for selection of appropriate economic technology. Indeed, the anticipated problems may influence the plans to develop a field, for example in terms of water injection strategies (eg sulphate reduction vs raw seawater injection)^{2,5} or implementing appropriate technology upon well completion (eg solid scale inhibitors vs continual injection capillary)³.

1.9.5 Scale Control Options

There are four principal categories of scale control options^{15,60}, as follows:

- Selection of injection fluid source
- Chemical inhibition
- Chemical/mechanical remediation
- Flow conformance

1.9.5.1 Selection of Injection Fluid Source

Injected water used for reservoir pressure maintenance and sweep may be incompatible with in situ reservoir brines, typically due to interaction of sulphate ions (in seawater or aquifer water) with cations in the formation waters. Injection fluid sources include⁵⁵:

- Full sulphate seawater^{1,3,9}
- Reduced or low sulphate seawater, using membrane technology
- Aquifer water
- Produced water Re-Injection¹⁷

The choice of source fluid is dependent on the availability of the potential sources of water, and the selection process should include a full evaluation of the scale risk within the reservoir, the production tubing and the surface facilities. From the scale risk (mass and location of scale) the economic impact to the CAPEX and OPEX costs can be evaluated.

1.9.5.2 Chemical Inhibition

Production wells can be prevented from scale formation by the addition of chemical inhibitors to the liquids upstream of the point at which scale starts to form. These chemicals prevent the nucleation, growth and adherence of scale, and may be deployed via three principal mechanisms^{54,60}:

- Batch (squeezing/fracturing fluid)
- Continual injection
- Impregnated solids

The choice of chemical inhibition is based on the scale risk assessment and the ability to place the chemical appropriately.

1.9.5.3 Chemical/mechanical Remediation

Production wells that have not been adequately protected may experience some degree of production impairment due to flow restrictions caused by scale. There are two primary methods of remediation

- Chemical dissolution (acids for carbonates and alkalis for sulphates)
- Mechanical (milling, jetting, explosives on string-shot, re-perforation and fracturing)

In general, chemical remediation is more efficient for carbonate relative to sulphate scale removal, but mitigation rather than remediation is usually regarded as more cost effective. Mechanical remediation methods are generally more effective than chemical, but typically involve greater expense.

1.9.5.4 Flow Conformance

The amount of scale that forms is a function of the concentration of scaling ions present and the volume of water produced. Reducing the volume of produced water would proportionally reduce the scale risk.

Options include:

- Chemical shut off (relative permeability modifiers¹¹, conformance gels, etc)
- Mechanical (sliding sleeves, straddle packers, downhole control valves, etc)

However, although these techniques may be used to reduce or delay water production, it is almost inevitable that the formation brines will find an alternative path to the well, and that the scale risk will not be eliminated.

1.9.6 Scale Inhibition Mechanisms

Since the main focus of this Thesis is the development of chemical scale inhibitors we will now address this aspect of scale control from 1.9.5 options above.

1.9.6.1 Nucleation and Growth

The formation brine present in a reservoir is assumed to be thermodynamically stable at reservoir conditions^{12,15,60}. Changes in pressure and/or temperature or mixing two incompatible waters will make the reservoir brine supersaturated. If a supersaturated brine is produced, the first stage of a scale-forming process is nucleation, either in solution (homogeneous nucleation) or on a substrate (heterogeneous nucleation). See Figure 1.16.

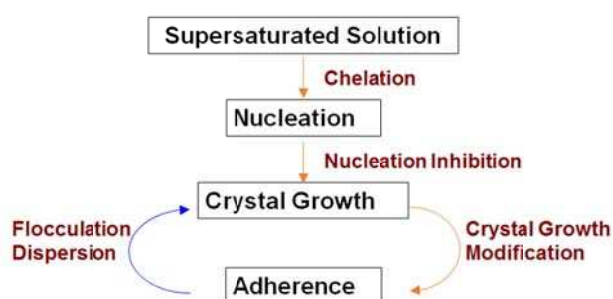


Figure 1.16 : Diagram to illustrate how scale can be controlled

Typical substrates in the oilfield include sand grains, clay and other minerals, metallic surfaces and scale crystals themselves.

The next stage in the process is crystal growth. The nucleons must reach a critical size before they are stabilized to form solid crystallites. This can only proceed after the nucleation has occurred, but once crystallites have been formed further nucleation is not strictly necessary for crystal growth to proceed.

Scale inhibitors must be able to prevent or delay crystal growth at the threshold concentrations. This means that it must be effective at sub-stoichiometric levels.

In describing the threshold effect, it is generally assumed that the inhibitor molecules adsorb at the active growth sites, which may be crystal defects, preventing further crystal growth by interfering with the growth process. Coupled with this, the morphology, tendency to agglomerate and the potential of the electric double layer (the zeta potential) of the growing nucleons can also be altered by the adsorption of inhibitor molecules at the growth sites. See Figures 1.17 and 1.18.

Nucleation inhibition

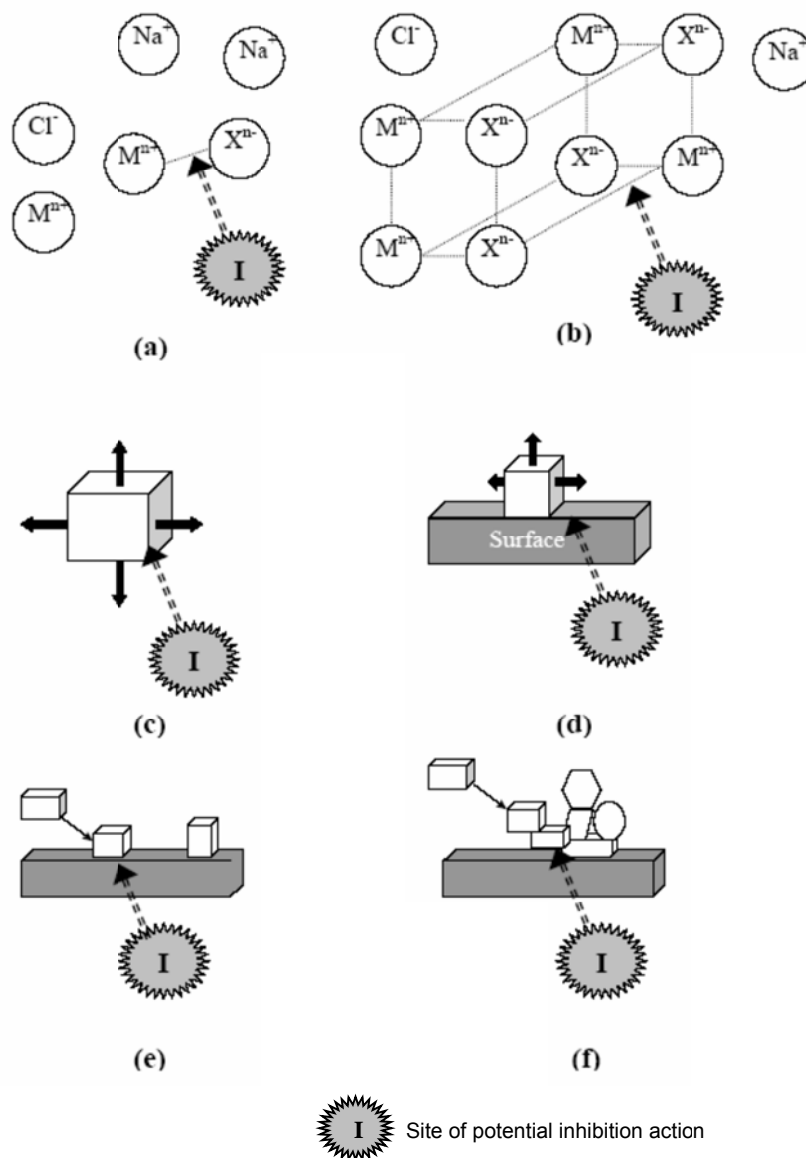


Figure 1.17 : Mechanism of growth and inhibition of scaling⁶²

- a) ion paring formation
- b) prenucleation cluster
- c) homogeneous nucleation and crystal growth
- d) heterogeneous nucleation
- e) crystal adsorption
- f) crystal conglomeration

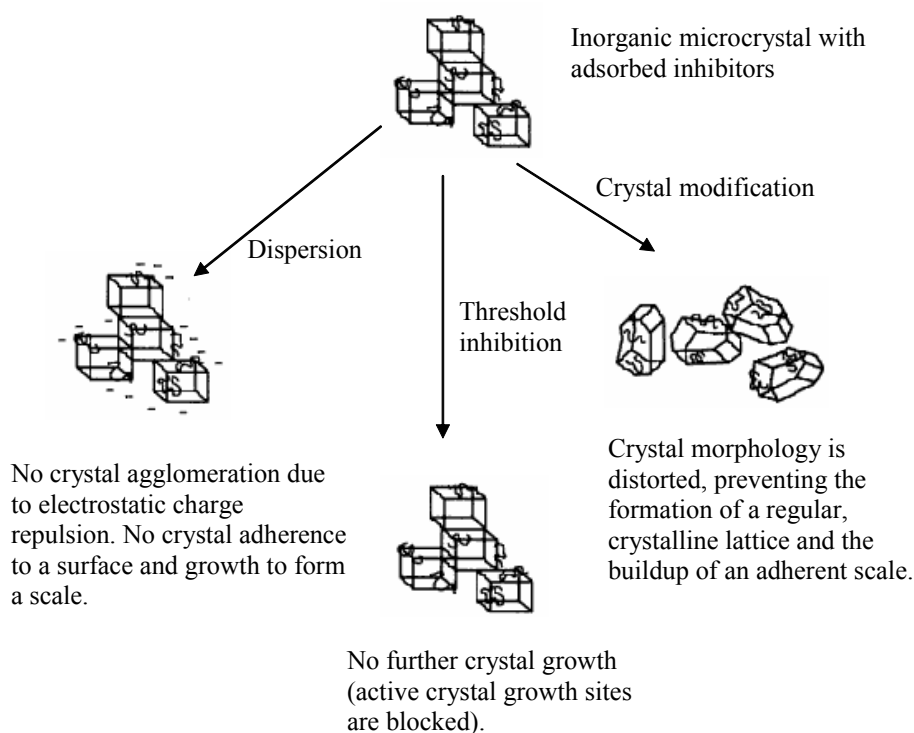


Figure 1.18 : Three major processes in the inhibition of scale deposition⁶²

Scale inhibitors interfere with nucleation, with crystal growth, or both¹²

1. Nucleation inhibition: By disruption of the thermodynamic stability of the growing nucleons. The mechanism of inhibition then involves endothermic adsorption of inhibitor species, causing dissolution of the barium sulphate embryo crystals. Inhibitor acts as nucleation site itself and chelates the scale formed in the aggregate.
2. Crystal growth retardation: Interference/blocking of the growth process of the growing crystals (for heterogeneous crystal growth). The mechanism of inhibition then involves irreversible adsorption of inhibitor species at the active growth sites of barium sulphate, resulting in their blockage. See Figure 1.18 above.

In the field, scale deposition is more likely to occur on the many surfaces which are already present in the system, eg in perforations, on tubulars, in valves and constrictions and on previously formed scale etc. In effect this means that it is extremely difficult to design a test which can satisfactorily simulate all possible scaling conditions in a well. Only experience from previous treatments in the well can give information about the inhibitor efficiency in the individual well.

For the inhibition of barium sulphate crystallisation, it is the dissociated (ionised) inhibitor functional groupings which interact with the growing crystal nucleus⁶⁰. The fundamental inhibition interaction is

an electrostatic process which, in turn, is affected by solution conditions such as pH. The solution pH dramatically affects the inhibition efficiency of the common phosphonate and polyacrylate based inhibitor species. This relates directly to the extent of dissociation of the inhibitor functional groups (ie the pKa values^{12,60}). Because several commonly used inhibitor species have weakly acidic functional groups (eg phosphonates, polyacrylates), they are dissociated at higher pH. At lower pH the phosphonates and polyacrylate based species are in their neutral form and are therefore less effective inhibitors.

Inhibitor species containing highly acidic groups (eg sulphonic acid groups as in PVS (poly vinyl sulphonate)) give good low pH inhibition efficiency.

An increase in calcium concentration results in an increase in inhibitor efficiency for most of the common inhibitors. The largest enhancement is seen with phosphonate based inhibitor species. Increased magnesium concentration appears to "poison" the phosphonate based inhibitors, but has little effect on the polymeric species like PVS and PPCA (phosphino carboxylic acid).

As mentioned earlier there are two principal mechanisms through which inhibitor species prevent scale formation; nucleation inhibition and crystal growth retardation. All effective inhibitor species act to some extent through both mechanisms although they mainly act through one particular mechanism as follows:

- Small polyelectrolytes operate primarily through a nucleation inhibition mechanism. Following initial nucleation, they continue to retard crystal growth, but do not appear to block growth completely and they therefore become less effective with time since they are consumed in the crystal lattice^{12,15,54,60}.
- Phosphonate species are less effective at preventing initial nucleation. However, once nucleation has started, they are very effective at stopping further crystal growth by adsorbing at active growth sites on the mineral scale crystal lattice. This initial nucleation results in a drop in supersaturation. The relatively high level of inhibitor remaining in solution is then sufficient to prevent further nucleation. Thus, after an initial drop in inhibition efficiency during the early (nucleation) period, they do not deteriorate significantly due to the operation of the crystal growth inhibition mechanism.

1.9.7 Application of Scale Inhibitors

If a risk of scale damage is predicted (or known to exist, from past experience) during a given operation, scale inhibitors are used. Scale inhibitors can be incorporated in drilling muds, completion brines, and process water. Continuous injection of scale inhibitors (at the well head) into production systems is commonly practiced to prevent scale deposition in process equipment. Scale inhibitors can also be combined with the gaslift gas or injected to ESPs via chemical injection lines. Also solid forms of scale inhibitors are available, as impregnated proppants for fracturing or gravel packs, or for dumping in the rat hole of the well or hanging off in baskets in the rat hole or below ESPs.

Batch (squeeze) treatment of production wells to prevent scaling in the near wellbore area and production tubing has become a routine operation for many operators.

Notes:

- a) Squeeze life can be extended by effecting precipitation squeezes where the chemical is mixed with a divalent metal in and allowed to precipitate in the warm reservoir. On backflow the dilution effect causes the chemical to dissolve and flow to the tubing.

Precipitation Squeezes

- Retention mechanism
 - Precipitation of inhibitor-calcium salt in formation pore throats
 - Dictated by:
 - Rock type (carbonate)
 - Product chemistry and pH
 - Water chemistry and pH
 - Bottom hole temperature

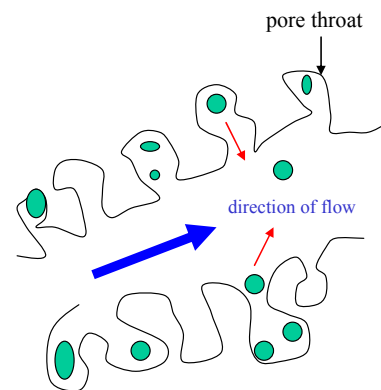


Figure 1.19 : Illustrates calcium polymer precipitates flowing into pore throats during squeeze⁵⁴

- Release mechanism
 - Controlled by isotherm coupled to solubility parameters & diffusion

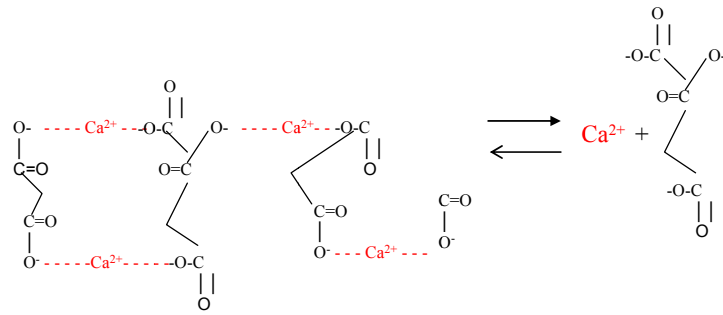


Figure 1.20 : Illustrate dissolution of the calcium precipitate during backflow⁵⁴

Adsorption Squeezes

- a) More commonly the squeeze life is extended by deploying chemicals which have a strong adsorption affinity for the rock through hydrogen bonding, electrostatic effect, Van der Waals forces. Figure 1.21 shows a proposed adsorption mechanism for a polymer.

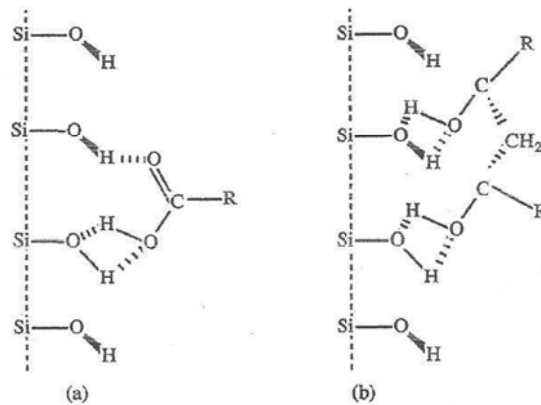


Figure 1.21 :

- a) Illustrates the polymer inhibitor⁵⁴ adsorbing to the silica of the reservoir rock surface
b) Increasing layers of adsorption.

The adsorption-desorption of an inhibitor to the formation is dependent on the strength of the inhibitor-formation rock associations

This can be defined by an adsorption isotherm which describes the chemical mass adsorbed onto the rock surface as a function of inhibitor solution concentration.

1.9.8 The Basic Field Squeeze Strategy

The chemical squeeze process is routinely used in oil and gas production and is recognised as providing one of the most effective and efficient methods of preventing the formation of sulphate and carbonate scale in producing wells and in new wellbore areas.

The basic process involved follows the steps which are illustrated in Figure 1.22.

1. **Preflush:** A pre-flush ($10\text{--}20\text{ m}^3$) which generally consists of a very dilute solution of inhibitor in water (normally seawater) and possibly some form of surfactant/oil-water demulsifier (acting mainly as an injectivity aid and possibly to increase the water wettability of the reservoir rock) is injected into the producer. This both cools and conditions the near wellbore formation.
2. **Inhibitor Injection:** The main inhibitor slug, generally consisting of 10-15% scale inhibitor dissolved in water (normally seawater), is injected into the near wellbore area. The volume of this slug depends on water rate and expected life time of the treatment.
3. **Overflush:** The main inhibitor slug is displaced to the required distance from the wellbore (normally 3-4 m) by injecting water (normally seawater). In low-pressure reservoirs diesel or nitrogen gas can be used as displacing fluid. This not only places the inhibitor slug deeper into the formation, but may, in addition, displace it from a "cool" near wellbore area into a hotter region of the formation.
4. **Shut-in:** The well will then be shut in for a specified period (normally 12-24 hrs) in order to allow the inhibitor to adsorb (interact) to the rock surface. Special consideration to shut-in time should be given if crossflow exists in the well.
5. **Back Production:** After the shut-in period the well is put back on production, and the inhibitor is expected to return to the wellbore at a concentration above the threshold level MIC (minimum inhibition concentration) for the design period.

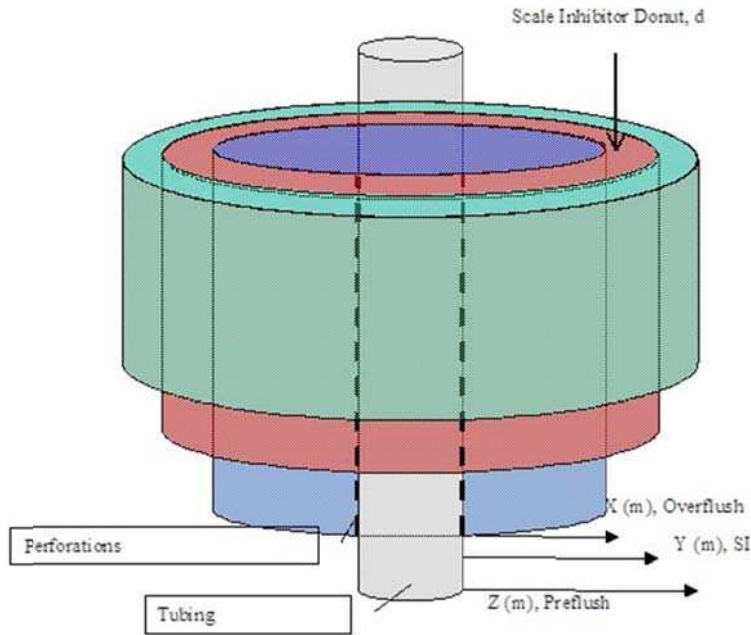


Figure 1.22 : Schematic illustration of the basic inhibitor squeeze with Spearhead Main Treatment and Overflush⁵⁴

The volumes of chemical deployed are decided by fairly basic calculations from field experience. The calculation bases the adsorption on one third of the chemical deployed actively adsorbing to provide a useful life of treatment. The basic diagram shows the radial distribution of the squeezed volume into the reservoir.

Two examples of how the volume of inhibitor is determined are given below. The first example shows the method utilised in the period from 1987-1994. The method reflects the experiences from the Murchison field. The second example shows the method applied later on NCS-fields⁵⁴:

$$1. \quad V(m^3) = Q_v \times D \times \bar{C} \times 3 \times 10^{-6}$$

Q_v : Expected average daily water rate during the expected squeeze life

D : Number of days expected squeeze life

\bar{C} : Average threshold concentration for the inhibitor (12 mg/l)

3 : Experience factor, indicating that 1/3 of the inhibitor is back produced immediately, 1/3 is irreversibly adsorbed in the reservoir, and 1/3 is available for scale inhibition.

$$2. \quad V(m^3) = Q_v \times D \times [MIC] \times F \times 3 \times 10^{-6}$$

Q_v : As in method (1)

D : As in method (1)

[MIC]: As in method (1), (5-8 mg/l depending on reservoir)

F: Flux factor*, varying from 1- 3 depending on water rate and perforation length

3: As in method (1)

*The flux factor, F, reflects the Champion experience that if two different wells are producing the same water rate, from 5 m and 40 m perforated intervals, respectively, the squeeze life defined as the time to MIC is shorter for the well producing from the 5 m interval if the same amount of inhibitor was injected, ie more water backflowing over the unit area of rock will remove the chemical (desorb) faster.

1.9.8.1 Inhibitor Placement

Successful placement of the inhibitor into the near wellbore area where the scaling occurs is crucial for a successful inhibitor treatment of a well. However, in vertical and deviated wells, most of the squeeze treatments are performed by "bullheading" the chemicals into the well. In extended reach wells, horizontal and multilateral wells, wells producing from more than one gravel pack and wells having cross flow or commingled production, more elaborated techniques are required, and squeeze treatment through coiled tubing, or "bullheading" applying chemical diverters (wax or oil soluble resins) will become important.

Successful squeeze treatments depend strongly on field experience and can be optimised either from examination of real field return data or from examination of field core flood return data. This involves the use of radial flow computer modelling programmes which are capable of taking into account inhibitor interactions with the near wellbore formation. The SQUEEZE VI model, developed at Heriot-Watt University can be routinely used for such applications^{12,13,14,69,70,71,72,73}.

Inhibitor propagation in adsorption/desorption squeeze treatments is related to the shape of the inhibitor adsorption isotherm, $\Gamma(C)$. This describes the relationship between the level of inhibitor

adsorption at the rock surface, Γ , (in mg/g or mg/m²) and the inhibitor concentration in solution, C.

When inhibitor adsorption/desorption reaches equilibrium, the propagation velocity of a given concentration C is given by the equation:

$$V_C = V_{fluid} / [1 + (\rho/\Phi)(\partial\Gamma/\partial C)]$$

Where: V_C = Velocity of a given concentration of inhibitor

V_{fluid} = Fluid (water) velocity

ρ = Rock density

Φ = Rock porosity

Clearly, the return velocity to the wellbore will be lowest when the factor $(\rho/\Phi)(\delta\Gamma/\delta C) \gg 1$.

Whether the adsorption is an equilibrium or non-equilibrium process, the underlying adsorption isotherm, $\Gamma(C)$, govern the form of the inhibitor return curve. For inhibitor adsorption, two forms of the isotherm, the Freundlich and Langmuir isotherms are generally used to describe the process⁷³.

The Freundlich Isotherm: $\Gamma = kC^n$ n is the isotherm index obtained from slope 's' of the log portion of the desorption curve [n = 1 + 1/s].

The Langmuir Isotherm: $\Gamma = \frac{abC}{1+bC}$

- a maximum absorption concentration
- C solution concentration
- b obtained from the gradient

Where k , n , a and b are constants. These constants can be altered in the mathematical model until values are obtained, which allow the particular return profile to be simulated. In this way inhibitor return data from core flood experiments can be used to design and optimize a field squeeze strategy. Adsorption/desorption characteristics are obtained from coreflood experiments and these data are input to the SQUEEZE VI simulator. Optimised squeeze treatments can then be modelled. Alternatively, inhibitor return data after a squeeze treatment are used as input to SQUEEZE VI and simulations can be used for further optimisation of the treatment^{69,70,71,72,73}.

A schematic view of how inhibitor core flood data can be used to design the field squeeze strategy is shown in Figure 1.23.

Note 1 Core data may not be representative of the 'field'. But its a start.

Note 2 The matching of history returns is more meaningful.

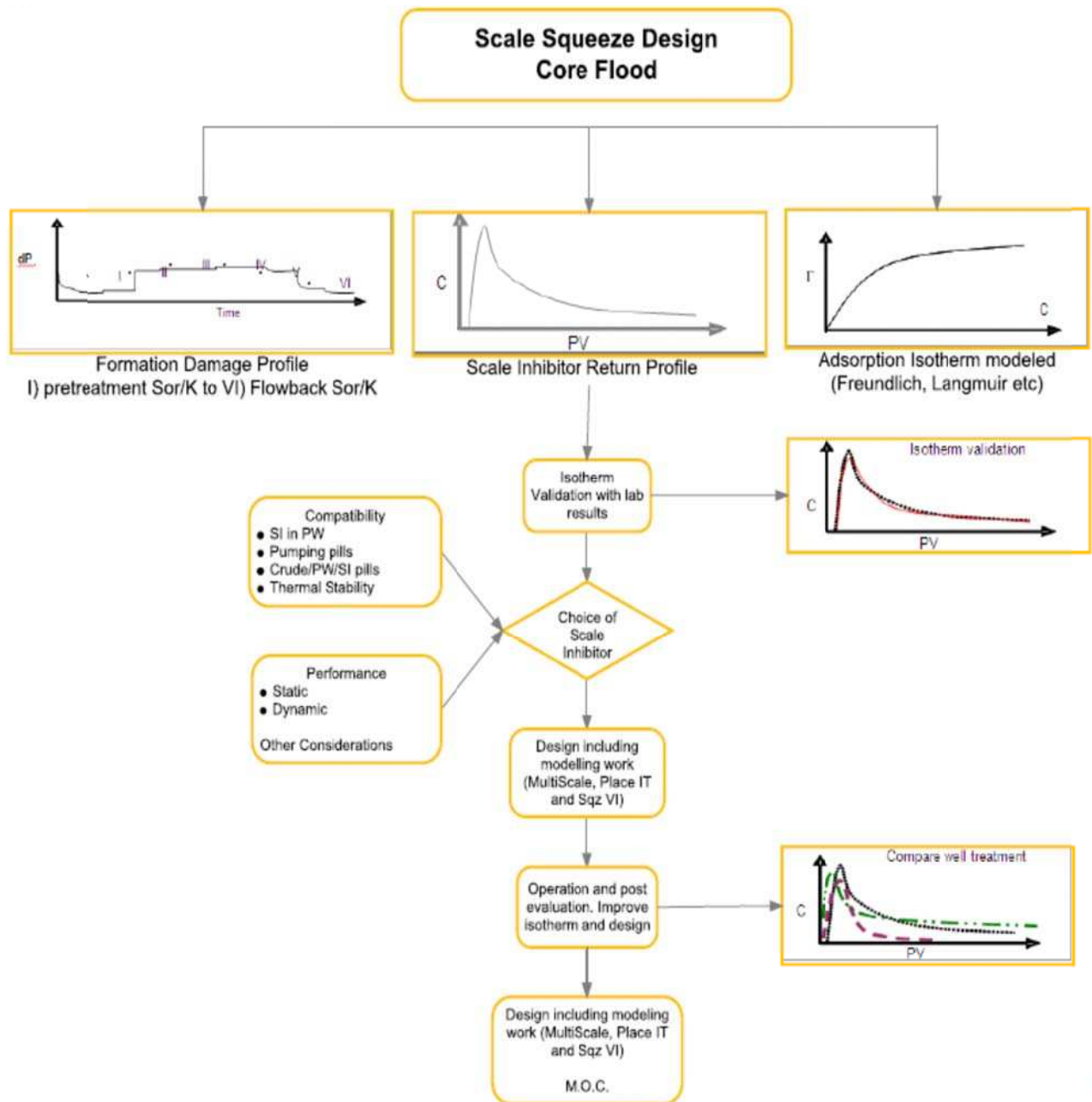


Figure 1.23 : A schematic view of how inhibitor core flood data can be used to design the field squeeze strategy^{12,13,14,54}

Once the correct parameters and isotherm references have been identified, adjustments to the particular squeeze design can be examined and the expected return profiles simulated.

The main point to notice is that for long low concentration returns the isotherm should be steeply rising in the low concentration region.

Note:

Formation Damage Profile – indicates the ΔP during coreflood tests. Ideally ΔP would have minimal deviation from start of test to the end when returned to permeability to oil/water. This indicates no damage to the core by the chemical.

Scale Inhibition Return Profile – indicates the return curve or desorption profile of the chemical. Ideally, the number of PV pore volumes would be high whilst the Concentration "C" (parts per million) of the chemical remained above the MIC minimum inhibitor concentration.

Adsorption Isotherm – indicates the modelling of the adsorption/desorption profile. This clearly demonstrates the adsorption of a chemical to the core of reservoir rock used in the test. The steep isotherm clearly indicates very strong rapid adsorption reaching a saturated high plateau. This is an ideal adsorption curve.

Isotherm Validation – indicates the actual field isotherm compared to the laboratory results.

Compare Well Treatments – indicates the life of treatments with, eg, differing squeeze designs or well conditions.

The isotherm can be used to study the "sensitivity" of the various elements of a squeeze, eg concentration of chemical, volume of chemical, overflush radius etc.

1.9.9 Scale Inhibitor Chemistry

The most effective and common approach to control the problem of oilfield scale, in particular that of barium sulphate, is through the use of chemical scale inhibitors. For downhole application scale inhibitors are injected into the near wellbore formation in a "squeeze" process. The two main properties required for scale inhibitors which are to be applied downhole are as follows^{12,15,60}.

- **Threshold inhibition:** These species must inhibit scale formation at very low sub-stoichiometric concentrations, typically at threshold levels of 1 to 15 ppm active inhibitor concentration. This level is also frequently referred to as the minimum inhibitor concentration (MIC).
- **Long squeeze lifetime:** The inhibitors must show long return profiles 3-12 months from the reservoir at levels higher than the required threshold concentration level ie minimum inhibitor concentration (MIC).

In considering the basic property of threshold inhibition which all scale inhibitors must possess, there are a number of a) structural features and b) influencing conditions, which directly control the effectiveness of inhibitor species. The main points are as follows:

- a) Structure features: include the following molecular attributes: Molecular weight, active functional groupings, hydrophobic content, stereochemistry (as relating to lattice matching) steric restrictions and flexibility, pKa values;
- b) Influencing conditions: relate to the following reservoir (and inhibitor treatment) attributes: pH, temperature, concentration of scaling ions, cation interaction in particular $[\text{Ca}^{2+}]$, gradients of the above pH/ $[\text{Ca}^{2+}]$, etc.

An important point to remember is the manner in which certain tests are performed. This will be described with regard to the comparative sensitivities of generically different scale inhibitors since the choice of test procedure can lead to conflicting results. It is therefore imperative that experimental procedures mirror as close as practically possible the exact nature of the scale control problem experienced in the field.

The common commercially available generic chemical types of downhole scale inhibitors are as follows: pentaphosphonate (DETPMP), hexa-phosphonates (Hexa-P), phosphino-polycarboxylates (PPCA), polyacrylates (PAA); poly vinyl sulphonic acids (PVS) and sulphonated polyacrylate co-polymers (VS-Co). The chemical structures of these species are in Figure 1.24.

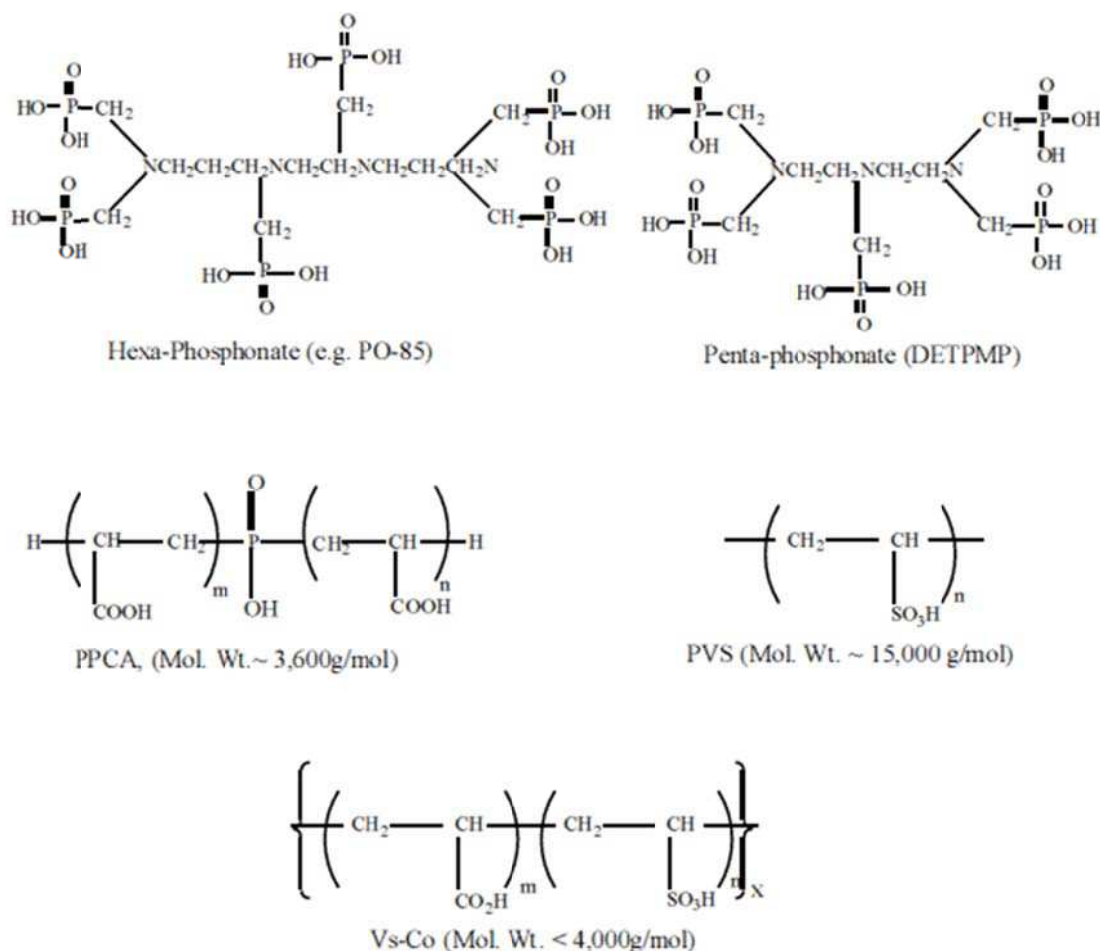


Figure 1.24 : Molecular structures of the different generic types of barium sulphate oilfield scale inhibitors⁶⁰

For inhibitors which are intended for downhole application, it is not sufficient that a particular species inhibit scale, it must also have the appropriate interaction with the formation to give sufficiently extended return curves, ie acceptable adsorption and desorption characteristics. In addition, the inhibitor must be compatible with the field brine and relatively stable to thermal degradation at reservoir conditions. Thus, a complete test programme to qualify a scale inhibitor should include an evaluation of its inhibition efficiency, its retention properties in the formation, its compatibility with field brines and its stability at reservoir conditions. Ideally, in order to assess potential formation damage properties, it may also be necessary to carry out reservoir condition core flood tests and compatibility tests with other chemicals.

Scale inhibitors have been used for more than 50 years. It is estimated that there are more than 2000 chemical scale inhibitors commercially available. However, today's oilfield scale inhibitors generally fall into two main classes:

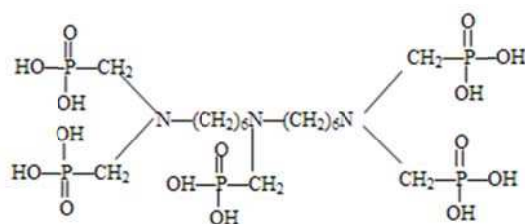
- organophosphorous compounds
- organic polymers

Scale inhibitor selection is based on at least inhibitor efficiency, chemical stability, compatibility with other chemicals and environmental testing. An acceptable scale inhibitor must be tested and meet the required limits for toxicity and biodegradability/bioaccumulation according to the rules given by the Governments.

Organophosphorous Compounds

The organophosphorous compounds can be sub-divided into two different classes of scale inhibitors. The first group are the organic phosphate esters. These chemicals are a natural progression from the inorganic phosphates and they still suffer hydrolytic instability.

The second group are the organophosphonates which are normally based on amines. These compounds contain the hydrolytically more stable -N-C-P- moiety and organophosphonates are now commonly deployed in the oilfield as scale inhibitors for sequestering calcium, strontium and barium ions. Other inhibitors within this group are phosphinopolycarboxylic acid and the later developed phosphonomethylated polyamines. For information BHMT and polyaspartate structures are shown below^{12,15,54,60}.



BHMT

(Bis Hexamethylene Pentakis Methylene – Phosphonic – Acid)

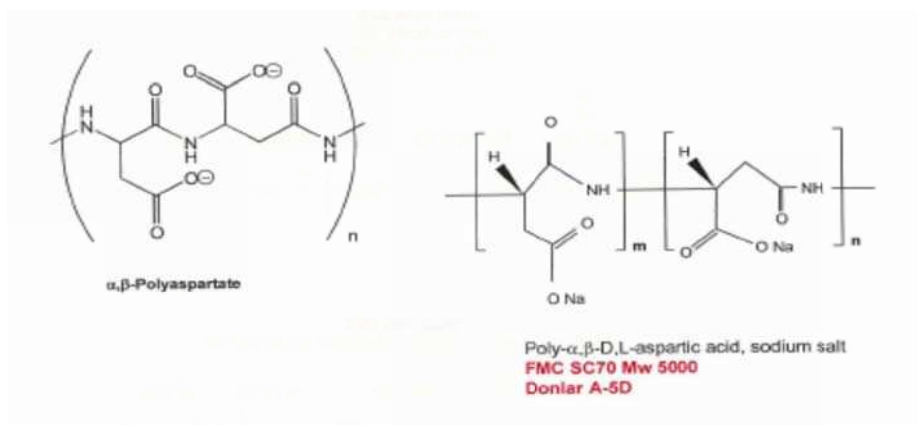


Figure 1.25 : Organic scale inhibitor molecules^{54,60}

Organic Polymers

Polycarboxylic acids are now becoming one of the most commonly used type of scale inhibitors. Effective polymers tend to have a low molecular weight (typically 1000-5000) and have regularly spaced active (ionisable) groups. These compounds normally have excellent thermal and hydrolytic stabilities. The most common classes of inhibitors include: polyacrylates, polymalates, polysulphonates and polyacrylamides. Poly aspartic acid has been tested as a combined scale and corrosion inhibitor.

The most important property that any scale inhibitor must possess is that it has the ability to prevent/inhibit crystal growth at threshold concentrations. This means that it must be effective at sub-stoichiometric levels.

The most widely used groups of downhole scale inhibitors for the control of BaSO_4 scale formation are phosphonates and small polyelectrolytes (molecular weight $<10^4$) with a polycarboxylate base. These inhibitors tend to show good performance over a range of pH and temperature conditions. However, their effectiveness deteriorates quite markedly as the pH is lowered^{12,15,42,43,60}.

For the phosphonates, the primary bonding mechanism appears to be an ionic interaction between the PO_3^{2-} group and the Ba^{2+} ions of the crystal growth sites. This is supported by the fact that the optimum pH for scale inhibitor performance is reached when the pKa value for $\text{PO}_3\text{H}^- \rightleftharpoons \text{PO}_3^{2-}$ is exceeded^{67,69,71}. In a similar manner, the primary bonding mechanism for polyacrylate based inhibitors appears to be an ionic interaction between COO^- groups and the Ba^{2+} ions of the crystal growth sites^{12,60}.

We conclude then that, for barium sulphate inhibition in the relatively high supersaturation brine mixtures generally found in North Sea environments, then it is the dissociated inhibitor functional groups that are required to inhibit scale formation. The mode of attachment is then by strong electrostatic bonding. For carbonate scales, since their formation is generally associated with a pH rise due to the loss of CO₂ from solution, we are generally dealing with higher pH systems (pH >5.5). In such cases the inhibitor molecules are expected to contain a high density of dissociated acid groups and once again strong electrostatic bridging mechanisms are responsible for the adsorption of inhibitor molecules onto the carbonate scale growth sites leading to scale growth inhibition⁶⁰.

1.9.10 Environmental Properties of Scale Inhibitors

Presently and in years to come the environmental properties of chemicals will be one of the major parameters in choosing products.

Norway has introduced the following parameters when mapping the properties of chemicals:

- Bioaccumulation (log Pow) of the different components in the products
- Biodegradation of the different components in seawater (%)
- Toxicity tests LC₅₀

For visualization it is customary to make a plot where the bioaccumulation is plotted against biodegradation.

A plot of this type is presented in Figure 1.26. The plot is divided into three different regions. Components that are located in the green area are classified as environmentally acceptable and can be used. Components in the yellow region shall be phased out and finally components, which are located in the red region, are not allowed to be used.

In the figure the environmental properties of the different components used for scale squeeze the last year are included. The figure proves that most of the components are located in the yellow region, which means that they are going to be phased out. This drives the need for new chemistry scale inhibitors.

PLONOR			
BOD $\geq 60\%$	if toxic \Rightarrow red	if toxic \Rightarrow red	
BOD $< 60\%$			if toxic \Rightarrow red
BOD $< 20\%$		if toxic \Rightarrow black	if toxic \Rightarrow black
	log Pow > 5	log Pow > 3	log Pow ≤ 3

Figure 1.26 : Environmental classification Norway SFT⁵⁴

CHAPTER 2
OVERVIEW OF PUBLICATIONS
CHAPTER 2 OVERVIEW OF PUBLICATIONS

The five papers included in this review demonstrate the R&D development process involved in selecting, deploying and monitoring downhole scale control in the oil industry. The necessary synthesis and manufacture of novel chemistry is also presented. The problems reviewed were not technically or commercially surmountable using the available products at that time.

Reference is also given to the Patents awarded.

Paper 1	SPE 80377	A way Beyond Scale Inhibitors – Evaluating Scale Inhibitor Squeeze Life Through Bridging.
Paper 2	SPE 100466	Field Experience in the Application of Inhibitor/Additive Interaction Package to Extend an Inhibitor Squeeze Life.
Paper 3	SPE 113926	Development of a New Polymer Inhibitor Chemistry for Downhole Squeeze Applications.
Paper 4	SPE 135249	Meeting the Challenges in the Downhole Scale Control of High-Water-Production Horizontal Wells in Environmental Sensitive Part of the Norwegian North Sea.
Paper 5	SPE 50706	Development of an Oil Soluble Inhibitor for a Subsea Satellite Field.

The order of presentation of the papers is designed to reflect the continuous improvement developments which took place in order to address the specific problems. The work although thorough had to be conducted almost against the clock since the oilfields were "in constant production" and had to cope with serious scaling issues causing potential millions of dollars damage and lost production.

The development story begins with a polyaspartate based scale inhibitor which performed poorly as a squeeze scale inhibitor on the basis of short squeeze life. It did however demonstrate the ability to control 'fines' and sand production in specific wells. This until then, unknown property was then studied and the polyaspartate used to extend the poor squeeze life of other polymers by the newly invented process of "bridging".

The project continued by focusing on improving the bridging properties by using a synthesised poly DADMAC (diallyldimethyl ammonium chloride) of selected molecular weight.

Finally the scale inhibitors, available at the time, which had poor environmental performance, short squeeze treatment life, poor barium sulphate inhibition coupled with difficulty in accurate residual analysis at the ppm (parts per million) level required of a squeeze scale inhibitor led to the industry demanding improved molecules be urgently developed.

The papers include the synthesis testing and deployment of the novel polymers successfully developed to address these issues.

2.1 SUMMARY

Managing inorganic scaling of produced water has been an ongoing challenge to the oil exploration and production industry. As the reserves become more rare the industry has been forced into developing more demanding reservoirs with HPHT, long horizontal wells and high barium connate water complicated by using seawater injection for pressure support. The authorities have also driven more environmental awareness by demanding treatments with low toxicity, high biodegradability and little or no bioaccumulation properties. This thesis has summarised the challenges encountered and the achievements produced when working closely with Statoil to overcome the difficulties. The papers focus on developing novel scale inhibitors and bridging technology for downhole scale treatments which solved the barium sulphate problems by using scale squeeze deployments. It should be noted that at the time, commercially available chemicals did not sufficiently address the challenges. Wells were being damaged and millions of dollars lost to irreversible damage, production downtime and intervention vessels costs.

The synthesis of new improved technology was the only way of improving the industry ability to control these scale problems.

Scale squeeze technology improvement demands are indeed significant. The chemicals require to address issues of scale inhibition, residual analysis accuracy, adsorption/desorption profiles, compatibility, stability at HPHT high pressure and temperature conditions and have acceptable environmental properties.

Paper 1 Describes the failure of a polyaspartate scale inhibitor which was highly biodegradable but which did not have a suitable adsorption desorption profile resulting in a very short squeeze treatment

life. The subsequent understanding of this unexpected effect on fines control and laboratory testing and validation in the field of the newly proposed 'bridging' package was then used together with a scale inhibitor product supplied by Rhodia to produce the treatment life required. The complete package also gave acceptable environmental properties and controlled the 'fines' problems.

The field deployments were accepted for use by the oil company and produced a 50% increase in the treatment life. Savings in excess of £9 million were achieved on one well alone.

Patents were awarded as described.

Paper 2 Describes future development of this novel bridging concept by testing other chemistries and shortlisting DADMAC or a suitable "bridging agent" with superior adsorption properties to the polyaspartate. The focus moved on to wells which were low in clay content sands and the difficulty in achieving acceptable squeeze life due to the lower adsorption properties of that rock.

The paper also describes in some detail, the development of a novel acrylate DADMAC copolymer scale inhibitor. The new molecules were synthesised and screened for barium sulphate inhibition in particular.

The adsorption characteristics of the synthesised copolymer were explored by using sand/crushed rock beaker tests as a quick screening method. The effects of pre-dosing the DADMAC molecule in the beaker test quantified its effect on increasing the adsorption of the scale copolymer. The negative relative permeability effects were noted in the core tests.

The copolymer synthesis had also successfully placed a 'P' (phosphorus)/tag on the molecule which could be measured accurately by ICP detection to <3 ppm (parts per million).

Finally, the products were successfully used in a specially designed squeeze deployment exercise in an offshore oilfield. The novel technology giving barium sulphate inhibition, fines control and extended squeeze life was patented and fully commercialised. The whole package was classified as environmental yellow by the Norwegian authorities.

Paper 3. The work continued to address the ongoing challenges of ever higher barium performance together with improved adsorption on rock both with and without the application of the bridging technology.

New acrylate DADMAC copolymers were synthesised over a range of molecular weights. Subsequent testing identified the best all round sample and some characterisation studies indicated the desired 'P' (phosphorus) tag was in place irreversibly and in significant quantity to aid residual analysis using ICP.

A series of tests indicated the copolymer was indeed performing as a good barium sulphate inhibitor and it also showed improved adsorption both alone and together with bridging technology. No adverse relative permeability effects were noted.

The products were successfully deployed in the field. To date over 40 field treatments have taken place with squeeze life exceeding 12 months, no oil water problems and good detection of return inhibitor concentration.

The package has a 'yellow' classification. Under these conditions no other commercially available products achieve this performance.

The technology was successfully patented.

Paper 4. The challenges of very high water production rates with longer horizontal well completions, serious barium sulphate (300 mg/l) and stringent environmental regulations were encountered. A non-damaging reservoir deployment was mandatory.

The synthesis of DADMAC based polymers was continued by focussing on achieving better barium sulphate inhibition performance together with compatibility characteristics. Compatibility with a third party provider's "gel" package was also mandatory.

Among the polymers synthesised were the terpolymer of acrylic, fumaric, DADMAC and acrylic maleic DADMAC of varying molecular weight and monomer ratios.

Subsequent laboratory testing barium sulphate inhibition, compatibility, adsorption, corefloods, gel package evaluations by Halliburton, led to the selection of a particular fumaric acrylic DADMAC terpolymer. Field deployments were successful to the extent the oil company did not subsequently require the 'gel' package component to achieve the squeeze life desired.

The product package was awarded a 'yellow' classification. The PI (productivity index) was unaffected by the squeeze process – if anything it improved. This product package is extensively used to this day and has controlled scale, minimised cost and met environmental targets.

The technology was successfully patented and controls scale in high water production wells.

Paper 5. The technical challenges addressed in this paper include designing downhole scale squeeze inhibition treatments which can be deployed in water sensitive reservoirs and or 'dry' wells or wells with very low water production.

The paper describes the development of a new oil soluble scale inhibitor and package which obviously does not introduce free water to the sensitive near wellbore areas. The laboratory tests and explanation of the unique properties of this new chemical are described. Properties identified include improved mass transfer from oil to water phases which is irreversible and enhanced partitioning.

No negative relative permeability effects were noted. The product hydrolyses and partitions to the connate water on the pore walls and then adsorbs to the rock. Since the partitioning back to oil is irreversible the product remains adsorbed until water breakthrough occurs. This gives the engineer proactive treatment possibilities and avoids the scale damage which usually occurs before scaling is detected and can be treated.

This work describes the first oil soluble scale inhibitors to be formulated and applied to solve problems in low pressure water sensitive oil reservoirs.

The technology was successfully deployed over a number of years and successfully patented. Statoil also began to patent the application for dry wells "on completion".

This oil soluble technology, in my opinion, should be further developed. Initial focus would be on environmental improvements to the package. The relevant copolymers and terpolymer described in Papers 1 to 4 have not been as yet studied for use in 'oil soluble' product development.

They could possibly bring good environmental properties, ease of analysis to <3 ppm residual level, excellent adsorption characteristics and leading edge barium sulphate inhibition performance.

A novel patented oil soluble scale inhibitor range has been developed for use in "dry" early well production and or water sensitive reservoirs. The products have been deployed successfully resulting in numerous papers and successful treatments of particularly water sensitive oil fields.

whilst delivering acceptable squeeze life have generally led to either formation damage through fines mobilisation, topside emulsion formation and/or are less environmentally acceptable.

A novel phosphorus containing end-capped polymer supplied by Rhodia was first deployed on Heidrun in January 2002, leading to increased squeeze duration. However, squeeze life was still short and fines mobilisation problems were still common and thus an alternative treatment strategy was required to maximise squeeze life and reduce fines mobilisation.

As a result of a joint R&D program an environmentally acceptable, multi-functional additive was identified to meet the challenges in extending squeeze life and effecting clay stabilisation on Heidrun. Additives were considered and evaluated for their potential to offer an environmentally acceptable treatment regime that extended scale inhibitor squeeze life. The laboratory procedures adopted to assess the suitability of the candidate additive to extend treatment life are detailed later in this paper. Finally, the mechanisms believed to be responsible for the effects of the additive on treatments both in the laboratory and in the field are discussed.

The publication describes the problems encountered on a North Sea oilfield, namely:

1. Loss of production immediately seawater break-through was noted which was identified as resulting in serious BaSO_4 scaling downhole.
2. Serious increased entrained oil in the produced water was encountered when a scale squeeze programme was initiated. This oily water issue was exacerbated by the injection of brines and chemicals loosening the poorly consolidated fines consisting of clays in the reservoir.
3. Subsequent difficulty in identifying alternative treatment designs and chemicals which also had acceptable environmental characteristics.

The paper describes the identification and design of the laboratory work procedures which were used to select the best available solution to both problems:

- a) BaSO_4 scale build-up.
- b) Fines released from rock causing oil water issues topside. It should be noted if oil in water is over 40 mg/l it is not allowed to be discharged into the North Sea.

The chemistries involved were phosphonates (industry standard) phosphate esters and various good Barium sulphate inhibiting polymers.

The latest developed scale inhibitor product up to then was a Rhodia manufactured proprietary end-capped phosphorous containing polymer. This polymer gave short squeeze life and worsened the oily water/fines issue.

The paper names the generic scale inhibitors selected as being the best identified so far and which were subsequently included in the lab tests to find an improved package.

During the field trials a polyaspartate based scale inhibitor had been deployed. It had been noted by the deployment team that the oily water production had not been an issue on the flowback as it had been with all the other chemicals. Unfortunately the polyaspartate did not have a long return profile and dropped below the MIC faster than hoped.

The data around all the polyaspartate deployments was closely studied and it was postulated that the chemical was working not only as a scale inhibitor but also as a fines/clay stabiliser^{16,17}.

Further research indicated that the polyaspartate was sold by the manufacturers (Donlar) to the agricultural industry. The polyaspartate is applied to the soil together with the fertiliser resulting in the longer retention of the largely water soluble fertiliser in the soil and subsequent longer period of crop being fertilised. Absence of polyaspartate from this process results in the fertiliser being washed away very fast by any rain. It is believed the small negative electrical charge on the polyaspartate allows it to attract to the soil which itself has an overall negative charge. The fertiliser then attracts to the polyaspartate by hydrogen bonding, van der Waals forces etc.

It was decided on this basis to study the effect of polyaspartate as a rock surface to scale inhibitor "bridging" agent in the lab experiments. It was named Additive F and consisted of Donlar polyaspartate sodium salt.

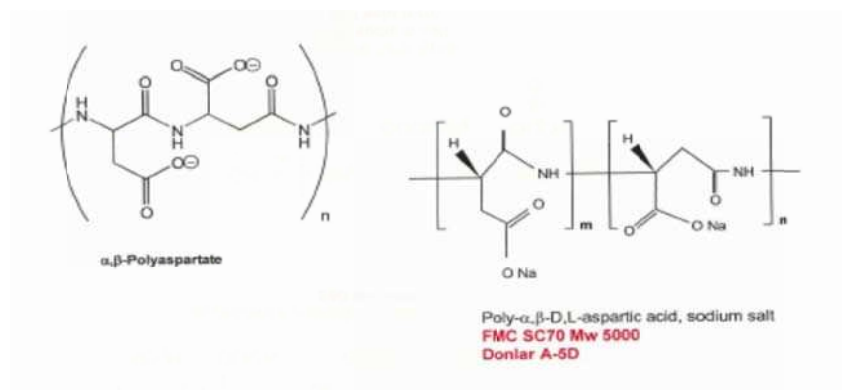


Figure 2.2 : Generic structure of polyaspartate

The idea was the polyaspartate would stabilise the fines but additionally modify the rock surface and present a more positively charged less repulsive surface to the negatively charged scale inhibitors. This would produce an enhanced scale inhibitor adsorption.

The Donlar polyaspartate "F" chosen for testing contained the desired functionality, to adsorb onto the more negatively charged rock surface, together with a suitable iso-electric point to present a more positive/less negative charge at low pH values. Product "F" has a low toxicity and high biodegradation (65%) and was classified as a 'Yellow' by Norway (SFT).

Experimental Overview

The scale inhibition performance of the products chosen was already known from previous work and deemed acceptable by the field engineers and the development team.

It was decided to focus on testing:

- a) Bridging concept 'beaker test' to study "adsorption" on crushed core or sand²⁵
- b) Enhanced adsorption dynamic core test.

Beaker Test

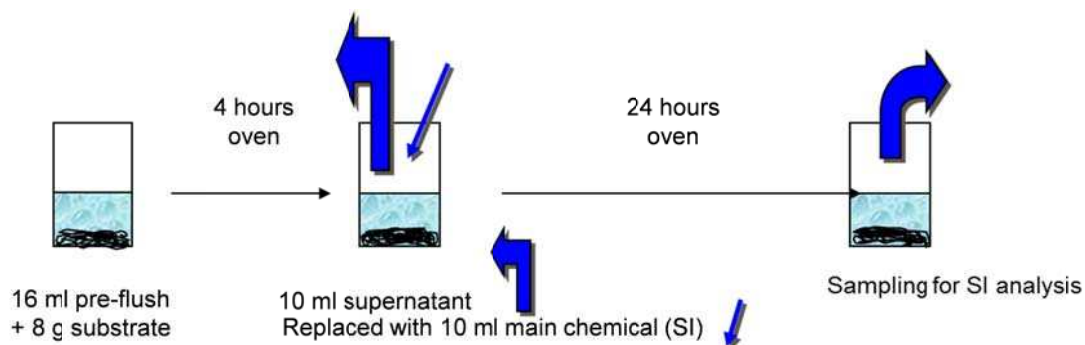


Figure 2.3 : Crushed core or sand adsorption test^{25,54,68}

- a) Crushed core from Heidrun field was prepared <2 mm size and allowed to dry
- b) Adsorption test (85°C)
 - The scale inhibitor and additive F solutions made up at 5000 ppm in 6% NaCl sodium chloride (w/w)
 - pH adjusted
 - 8 grams of crushed core added to HDPE bottle (60 ml)
 - 16 ml additive F mixed with crushed core in bottle, 4 hours in oven at 85°C

- 10 ml of the supernatant liquid removed and replaced by 10 ml of the scale inhibitor solution
 - 24 hours later concentration of inhibitor in supernatant liquid analysed.
 - Adsorption calculated.
- c) Adsorption test repeated but with 6% brine only – no additive "F" at first step
- d) Blanks tests run as reported.

Results

The crushed core test indicated that all tested products increased adsorption when additive F was present. Product A was clearly best as expected of a pentaphosphonate.

This gave confidence to go ahead with the coreflood tests.

Sample	Pre-conditioning	Inhibitors	Adsorption mg/g	% increase in adsorption
1	NaCl 6%, pH =3	Inhibitor A at pH 3	4.53	
2	Additive, pH =3	Inhibitor A at pH 3	4.91	8.44
3	NaCl 6%, pH =3	Inhibitor A at pH 5	3.82	
4	Additive, pH =3	Inhibitor A at pH 5	4.04	5.87
5	NaCl 6%, pH =3	Inhibitor B at pH 3	1.68	
6	Additive, pH =3	Inhibitor B at pH 3	1.85	9.87
7	NaCl 6%, pH =3	Inhibitor B at pH 5	1.59	
8	Additive, pH =3	Inhibitor B at pH 5	2.01	26.61
9	NaCl 6%, pH =3	Inhibitor C at pH 3	3.17	
10	Additive, pH =3	Inhibitor C at pH 3	3.19	7.07
11	NaCl 6%, pH =3	Inhibitor C at pH 5	2.87	
12	Additive, pH =3	Inhibitor C at pH 5	3.16	10.09

Table 2.1 : Enhanced Adsorption of Scale Inhibitors A-C

Coreflood Tests

Industry standard core flood procedure adopted.

Clashack outcrop used. Brine was recreated Heidrun but SO_4^{2-} ions not included.

Filtered through 0.45 μ membrane.

pH 6.5 prior to injection.

Coreflood procedure was industry standard in terms of equipment and methodology.

Two corefloods were run. The first with additive F preflush before scale inhibitor. The second coreflood had scale inhibitor alone injected.

The product D was chosen for the coreflood based on its biodegradation (25%) being far superior to the other A, B, C products. This is an indication of the time and environmental constraints faced by the development team at that time. The coreflood resulted in product D desorption curve improving from 100 to 180 pore volumes before 1 ppm was reached. See Figure 2.4.

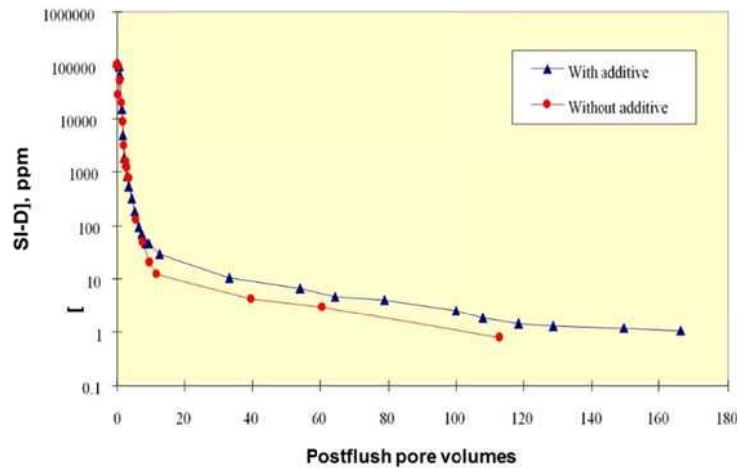


Figure 2.4 : Scale inhibitor D return profiles obtained from core floods with and without multi-functional additive F preflush

Field Data

Data from numerous squeezes on Heidrun are available. Figure 2.5 shows the scale inhibitor return profiles for phosphonate, polyaspartate and end-capped polymer with and without additive F.

Treatment 1 (phosphonate) return profile shows uncharacteristic drop at around 17000 m³. It is postulated this was due to return fines particles adsorbing the chemical and being either dropped out or filtered out before the ICP run, giving the lower residual ppm result.

Indeed, stabilising and controlling fines and or sand production by the additive will impact positively on the squeeze life by minimising the loss of inhibitor adsorbed on fines which become mobile.

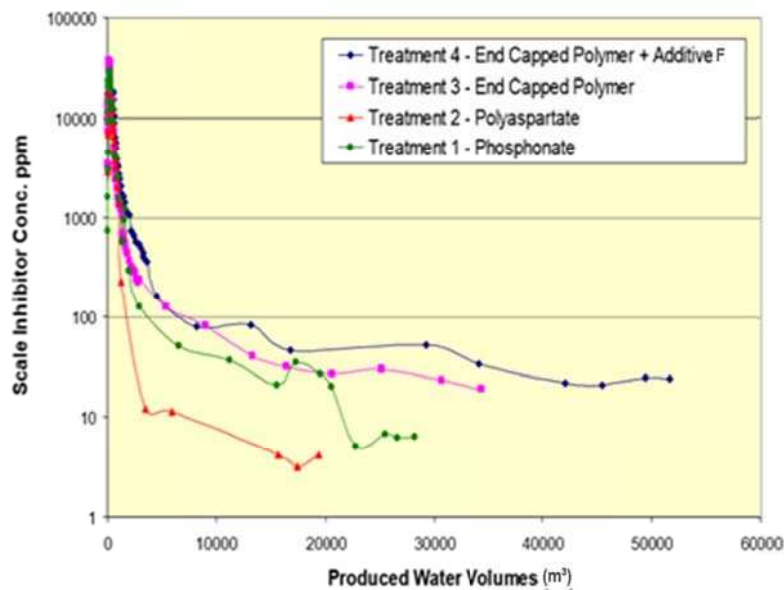


Figure 2.5 : Scale inhibitor return comparison for treatments 1-4

Treatment 4 clearly demonstrates the improved performance when additive F is present.

SPE 80377, Table 3 shows the squeeze life data (as produced water volume) for phosphonate/polymer/copolymer plus additive F. Note the MIC 24 ppm is required to inhibit the water chemistry present at the time (increasing SW breakthrough).

SPE 80377, Table 3 also clearly shows the increasing performance of the selected products as scale inhibitors, ie MIC vs vastly more difficult scaling scenarios involved. It also becomes obvious that the worsening scale potential as SW increasingly breaks through is demanding that an improved performing scale inhibitor is developed.

Squeeze Modelling

Heriot-Watt have developed and continue to refine and improve a modelling program (Squeeze V) which allows data for squeeze deployments and indeed coreflood data to be graphically represented and also to allow the user to manipulate the different inputs to check their sensitivities. This allows improvements to be made in the design and deployment of future scale squeeze exercises¹⁸.

Treatments 3 and 4 return data were loaded into Squeeze V. SPE 80377, Figures 3 and 4 show the return ppm vs time. SPE 80377, Figure 4 clearly shows a much improved profile, is obtained when using 'F' as a preflush.

The modelling clearly showed a Freundlich Isotherm gave a good fit for this data. SPE 80377, Table 4 shows the parameters k, n and r2 values for both treatments:

k	for treatment 4 is	1200 vs 800 for treatment 3
n	for treatment 4 is	0.4 vs 0.16 for treatment 3
r2	for treatment 4 is	0.11 vs 0.29.

Note: k and n indicate higher levels of adsorption for treatment 4 while r2 the adsorption rate constant indicates a lower adsorption/desorption rate for treatment 4.

The mathematical model demonstrates improved desorption profile with additive F preflush.

Clay Stabilisation (also known as Fines Stabilisation)

We have already discussed the properties of additive 'F':

1. Some scale inhibiting ability
2. Fines/clay stabilisation
3. Squeeze life extension by providing improved adsorption for the scale inhibitor package.

A brief review of the field data is presented.

It is normal to express well productivity as PI the productivity index which is calculated as a measure of pressures and flowrates.

For a dry well producing above bubble point we calculate the PI in SM³/day/bar as⁵⁴:

$$PI_o = Q_o / (P_r - P_{wf})$$

Where Q_o is the oil rate SM³/day

P_r is the reservoir pressure bar

P_{wf} is the well flowing pressure bar.

Ideally we graph PI vs time for each well.

SPE 80377, Figure 6 shows PI dropping from 35 to 16 after a well scale squeeze on 28 October 2000.

After reviewing other possibilities, eg precipitation of non-compatible inhibitor package and reservoir rock and or fluids it was decided clay migration was the cause.

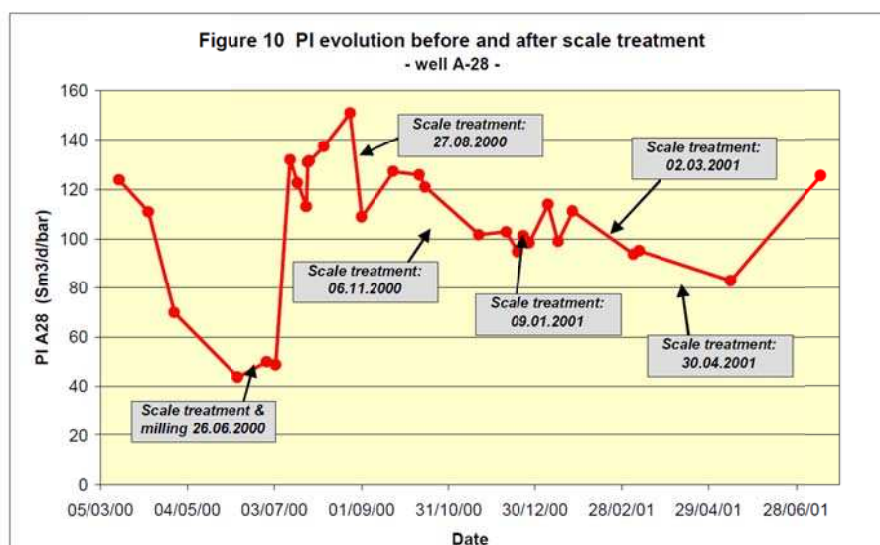
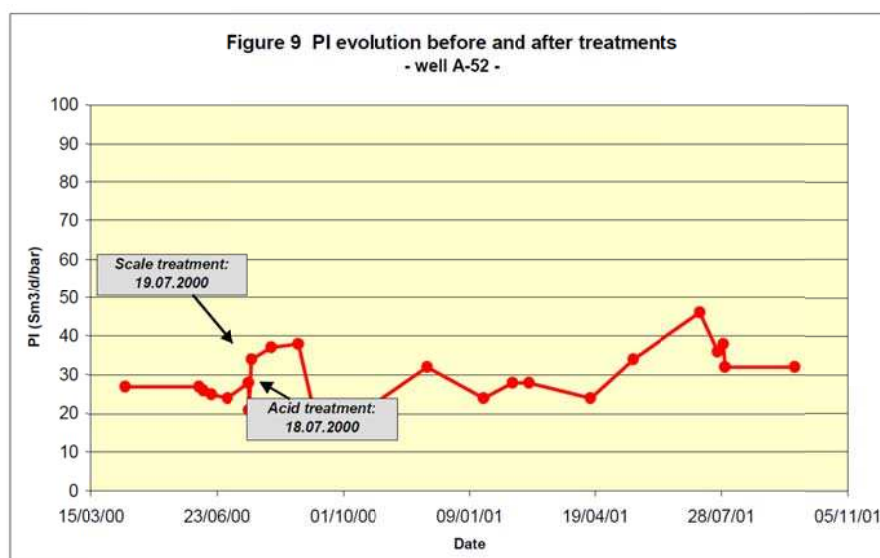
Clays can be destabilised and encouraged to become mobile with the produced fluids when exposed to change in brine salinity, chemistry, pH and non-native chemicals and indeed changes in flow rate.

This movement is thought to be caused by disruption of the forces binding clay and sand particles in the reservoir. The moving particles can then be deposited/strained out in capillary constrictions or plug pore spaces. Ultimately reduced permeability is achieved. Selected polymers¹⁹ can coat the rocks including the clays particles and help them stay adhered to each other reducing tendency to be mobilised^{20,21}. Clay swelling can also have negative flow impact. Swelling is exacerbated by different brines, pH and surfactants.

SPE 80377, Figures 7 and 8

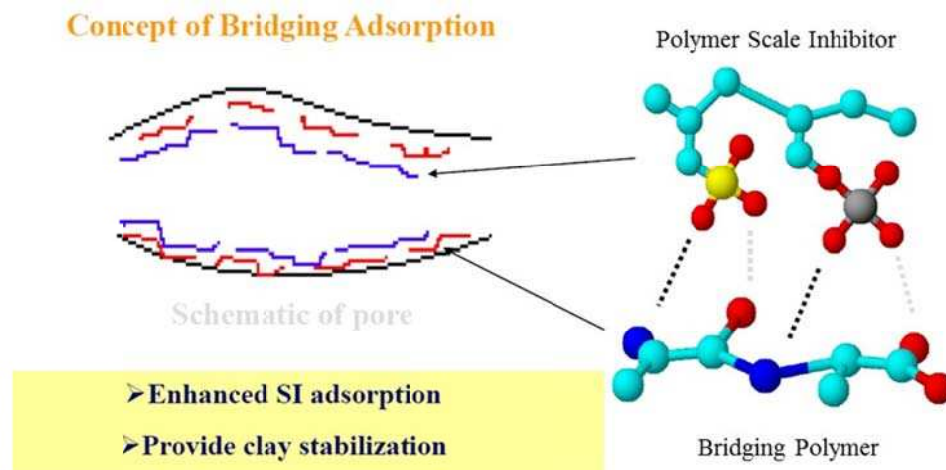
PI drops after water breakthrough. This was presumed to be clay migration. An acid stimulation was effected which increased the PI giving recovered oil production rates.

However, when scale squeezes were then deployed PI immediately decreased.



SPE 80377, Figures 9 and 10 (reproduced above)

Following acid wash and scale milling respectively the wells were treated using the additive F and scale inhibitor. The PI data improved in both cases over time to above 40 over some months for well A52. Well A28 (Figure 10) was subjected to 6 scale inhibitor squeeze treatments over 16 months. All treatments used the additive F package. No significant impact on PI was experienced.



Bridging agent concept to improve scale inhibitor adsorption⁷⁴

Conclusions

1. Heidrun field presents a challenge in scale inhibitor and fines/clay control
2. Numerous aqueous squeezes and non-aqueous scale inhibitor treatments with many different chemistries have been deployed. In most cases fines movement, oily water and production losses have been experienced.
3. An R&D effort identified 'bridging and' additive F which enhanced the adsorption and the squeeze life of otherwise limited Rhodia scale inhibitors and additionally controlled the clay/fines problems
4. The additive also demonstrates scale inhibition and is environmentally acceptable.
5. Field trials have proven the laboratory data
6. Squeeze V indicates the 'F' additive effected greater adsorption of the scale inhibitor but at a slower rate. The plus is it also desorbs at a lower rate. The well backflow residuals analysis has proven the improved desorption rate/profile is ideal for scale inhibition using numerous polymers which otherwise would have very short squeeze lives.

7. The deployment of the additive resulted in a 50% increase in treatment life with annualised deferred oil saving of 72,500 standard cubic metres valued at over £9 million on one well alone. Massive savings in chemical and treatment costs with the resultant need for less than half the interventions is not captured here.
8. Patent PCT/GB2007/003131 awarded.

2.3 PAPER 2 SPE 100466

"Field Experiences in the Application of an Inhibitor/Additive Interactive Package to Extend an Inhibitor Squeeze Life." SPE 100466 Journal of Foreign Oilfield Engineering Vol 24 No.4 2008. PCT/GB2007/002877

2.3.1 Development of new polymer scale inhibitor

This paper presents a continuation of the technology evolved previously and discussed in Paper 1. The polyamine acid (polyaspartate) treatment earlier developed and reported has provided improved squeeze life and fines control during multiple well treatments. However, it was decided to develop an improved chemical treatment which would be more effective in extending squeeze life in non or low clay bearing rock reservoirs. A major consideration was the requirement to produce a biodegradable low toxicity chemical. The goal was to synthesise both improved scale inhibitors and improved bridging/fines control chemicals.

Several publications have outlined both the experimental and field data as well as treatment designs to develop "green" scale inhibitors and additives to extend squeeze life^{22,23,24}. This paper describes the development of a novel inhibitor and extender package.

A literature review^{64,65,66} indicated good squeeze lifetimes demand good inhibitor adsorption. The mechanism can include adsorption and precipitation. Many factors influence the adsorption, eg the inhibitor chemistry and charge and concentration, brine, pH, temperature and rock mineralogy. At lower pH the weakly acidic scale inhibitor will be more protonated and can be retained on the rock surface by hydrogen bonding and Van der Waals forces. Higher pH scenario indicates the scale inhibitor will be more dissociated and will be retained by weak Van der Waals forces, and electrostatic forces due to metal cation bridging.

Many research studies have been focussed on improving the squeeze life. Adding calcium ions has been shown to be effective²⁵. This process has been referred to as surface precipitation.

Precipitation squeezes have also been developed using added Ca^{++} to extend the life. Here the Ca ions have complexed with the scale inhibitor and at specific temperature and pH a precipitate forms^{26,27}. There was indication of loss in permeability to oil and brine. This is obviously not acceptable since it causes impaired production and irreversible well damage, both costly to the oil companies.

Many other methods have been evolved to extend inhibitor squeeze lifetimes:

- Ester cross-linking of polycarboxylic scale inhibitor²⁸.
- Miscible displacement method²⁹ involved oil in water micro emulsion
- Positively charged additives adsorbing to the largely negative charged rock surfaces^{23,30,31,32} and subsequently bonding/bridging with the scale inhibitor.

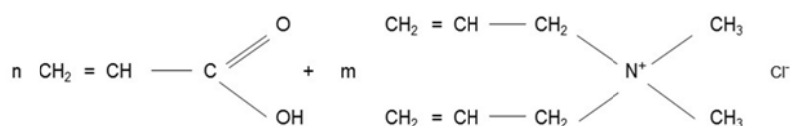
This paper is focussed on testing a newly formulated scale inhibitor and an improved squeeze life extender.

Scale Inhibitor Development

The adsorption and clay stabilisation properties of poly DADMAC have been widely leveraged by the drilling companies. The molecule itself is quite reactive and easy to polymerise with other monomers. We decided to focus initially on its reactions with acrylic acid since the properties of polyacrylic acid as a scale inhibitor are widely known. The plan was to then, if successful, to react with different monomer(s) known to have scale inhibition properties eg SO_3H (sulphonates) and fumarates.

Note 1 - The novel DADMAC acrylate chemical was developed by preparing numerous molecules derived from reacting monomer diallyldimethyl ammonium chloride (DADMAC) with anionic monomer acrylic acid and or vinyl sulphonic acid.

It should be noted numerous combinations were synthesised using the solution polymerisation technique with sodium or ammonium persulphate initiator (1-2% of monomer weight) and chain transfer agent hypophosphorous acid (2-5% of total weight) or sodium hypophosphite



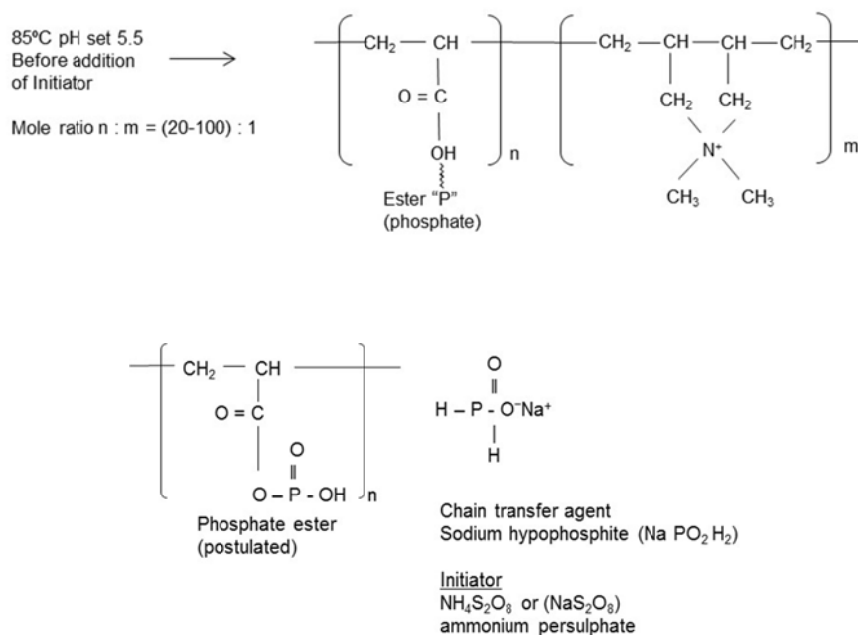


Figure 2.6 : Reaction pathway for DADMAC acrylate

Notes

1. P attaches as ester to COOH group. Also can be attached to end chain of polymer.
2. To achieve 1 ppm P in final product it is required to have 200 ppm in the polymer molecule.
3. Chemistry Patent granted PCT/GB2007/003131

Experimental

Performance Test

Having achieved stable reproducible 'new molecules' it was decided to performance test them as scale inhibitors.

Dynamic Scale Loop

See Figure 2.7 "the dynamic scale flow loop".

The loop is designed to assess ability of inhibitor to delay scale growth and set minimum inhibitor concentration (MIC)

This rapid screening test examines:



- Performance over 2 – 6 hours
(typically- specific to test)
- Range of water chemistries and temperatures
- Range of products and concentrations
- Evaluation through ΔP interpretation

- Method:

The waters to be tested are usually:

- i) produced or formation water
- ii) above mixed with seawater,
- iii) ratios of i) and ii).

Notes:

- a) The brines are made up as cation and anions calculated to give the final mix to be studied usually based on pumping 50:50 of the synthetic anions and cations.
- b) The brines are made up separately as anion/cation to prevent scaling prior to mixing in the apparatus coil or loop
- c) Any sulphate SO_4^{2-} (as Na_2SO_4) is added to the anion brine as is bicarbonate (NaHCO_3)
- d) If pH needs adjusted HCl is added to cation brine and NaOH to the anion brine

- Synthetic brines made up: Cation and Anion
- pH of the 50:50=Cation:Anion adjusted or at least measured
- Temperature and back pressure set
- Cation and Anion pumped separately and heated in heating coils
- Cation + Anion mixing at T junction just before entering scaling coil. See Figure 2.8
- Differential pressure ΔP measured across scaling coil
- ΔP increases when scale forms and blocks the coil
- Criteria of Fail is when ΔP increases by 1 psi over the test period
- Blank test recorded first
- Scale inhibitor tests with SI (scale inhibitor) dosed in one of the brines (usually Anion)

- Test time is typically 2-3 times Blank time with no scaling,

Schematic loop apparatus

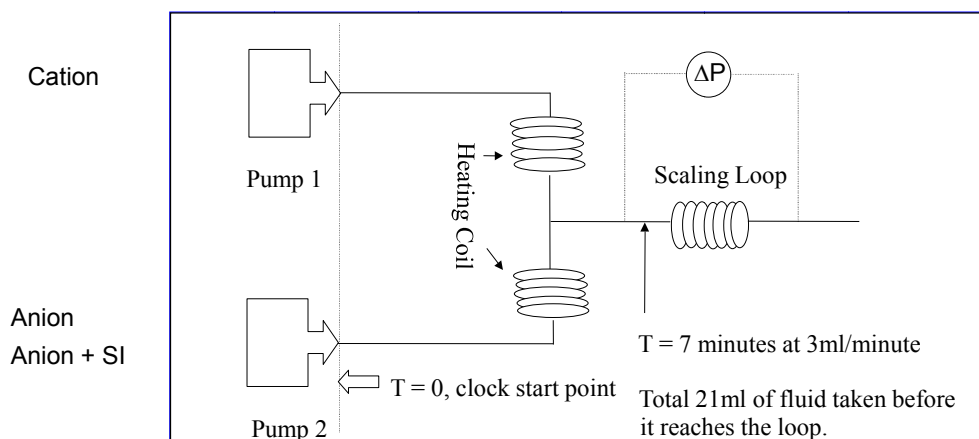


Figure 2.8 : Schematic of scale dynamic loop⁵⁴



Figure 2.9 : Dynamic loop showing the coils inside the oven⁵⁴

Dynamic loop tests were conducted in order to evaluate the performance of the DADMAC (diallyldimethyl ammonium chloride) and acrylic acid copolymer in scale control. Loop tests using a known polyacrylate polymer as a scale inhibitor were also carried out for comparative purposes.

The brines used in the studies were synthetic Heidrun formation water, seawater and a 6% NaCl brine made from dissolved salts. The compositions of these brines are given in Table 2.2.

Composition (mg/l)	Heidrun Formation Water	Seawater
Na ⁺	19510	11150
K ⁺	545	420
Ca ²⁺	1020	428
Mg ²⁺	265	1410
Ba ²⁺	255	0
Sr ²⁺	145	0
SO ₄ ²⁻	0	2800
Cl ⁻	33190	20310

Table 2.2 : Composition of Brines

The dynamic scale inhibitor performance test is designed to evaluate the ability of the test inhibitor to delay the nucleation and growth of scale on a pre-scaled metal surface. All tests were performed with mixed brines, ie 50:50 Heidrun formation water: seawater (see Table 2.2). The test conditions were designed to represent an extreme case of barium sulphate scaling.

A schematic of the equipment used is presented in Figure 2.8. In the tests, the formation water and seawater were separated into non-scaling cation and anion brine fractions such that on mixing the anion and cation brine fractions the mixed brine would be representative of 50:50 mixed formation water and seawater. The barium is present in the cation brine and sulphate is present in the anion brine. The two brines were pumped separately into the heating coil using two pumps (this ensures the fluids reach the test temperature before they mix in the loop). After passing the heating coil, the cation and anion brines were then mixed at the T-junction of the inlet of the scale loop. The formation of scale within the scale loop was tracked by measuring the differential pressure changes across the coil as a function of time. Scale inhibitors are designed to prevent the adhesion and growth of scale within the scale loop and thus prevent an increase in differential pressure at a particular concentration. This is termed the minimum inhibitor concentration (MIC) and is stated in ppm (parts per million).

The transport time for the anion and cation brines prior to mixing was 7 minutes at a pump rate of 3 ml/minute. This represents a dead volume of 21 ml of total fluid, pumped by each pump.

The test conditions were set as below:

Temperature	85°C
Ambient pH of mixed brine	6.5 ± 0.3 (adjusted with 0.1 M NaOH)
Coil length:	1 m
Coil internal diameter	~0.9 mm
Flow rate:	14 ml/min

Following each test, the loop was cleaned with 50 ml scale dissolver, 50 ml deionised (DI) water, 50 ml 1% acetic acid solution then DI water until pH = 7±1.

The lowest inhibitor concentrations to inhibit scale formation for 3 hours are shown in Figure 2.10 for inhibitors according to the present invention and Figure 2.11 for polyacrylate inhibitor used as reference.

The plots in Figures 2.10 and 2.11 show the differential pressure measured vs time. In Figure 2.10 the line marked "Blank" represents the test without scale inhibitor where scale quickly built up inside the coil resulting in a steep increase in the differential pressures. The grey lines represents the test where 15 ppm of scale inhibitor was present in the mixed brine. The differential pressure increase was delayed due to the presence of 15 ppm of scale inhibitor. The black lines represent the tests at 20 and 25 ppm scale inhibitor respectively. Both black lines clearly show that when the inhibitor concentration was increased to 20 and 25 ppm, the barium sulphate scale precipitation was well controlled, resulting in stable differential pressure readings. In contrast, Figure 2.11 shows that at least 35 ppm polyacrylate inhibitor are required to control barium sulphate scale precipitation.

The dynamic loop tests demonstrate that the polymer material of the invention is an effective scale inhibitor under North Sea reservoir conditions. Under the given conditions where the barium concentration is as high as 255 ppm, the scale inhibitor can control the barium sulphate precipitation in the dynamic loop at 20 ppm over a 3 hour test interval.

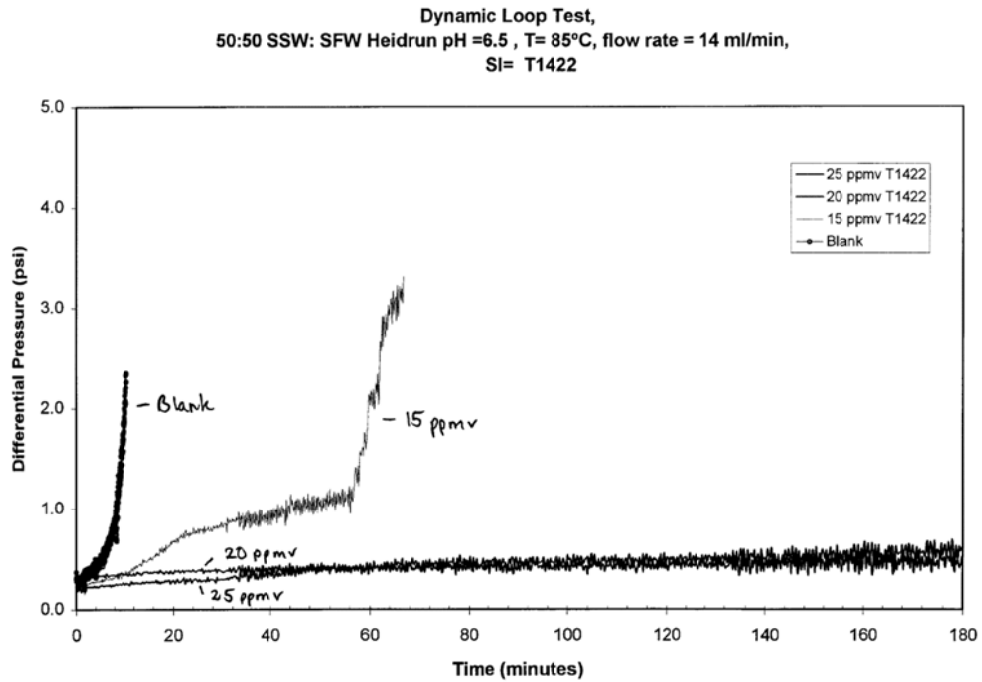


Figure 2.10 : ΔP Plots showing increasing ppm treat rates of T1422

Note: T1422 is DADMAC acrylic copolymer.

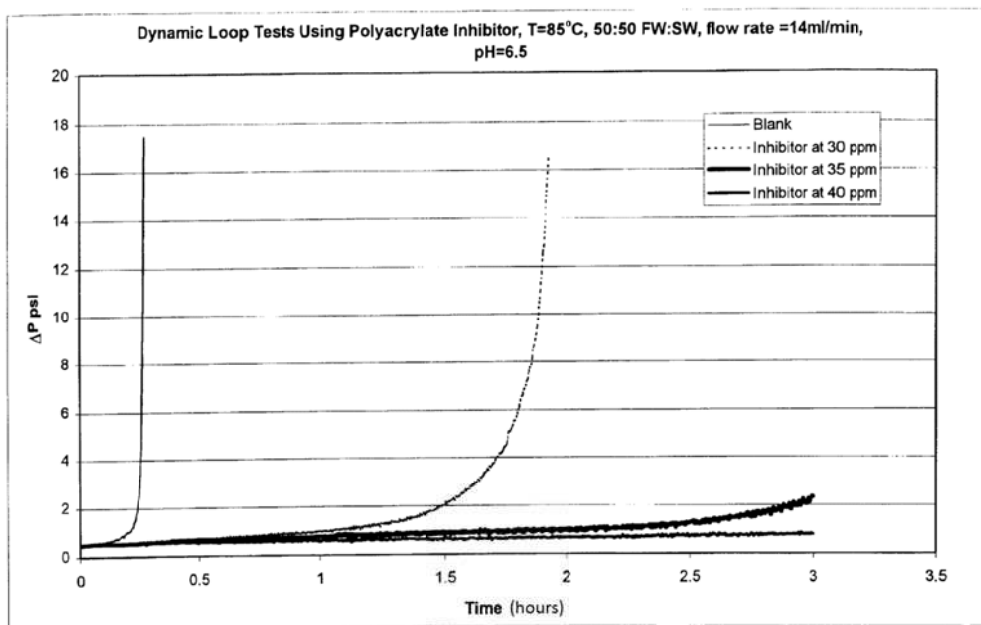


Figure 2.11 : ΔP Plots showing increasing ppm treat rate of standard polyacrylate

Conclusion

1. A novel DADMAC acrylate copolymer has been developed.
2. The T1422 version of the new molecules outperforms an industry standard scale inhibitor in dynamic flow loop tests where the barium sulphate condition was severe.
3. The initial environmental tests gave indication of biodegradation in excess of 40% which at that time was 'Best in Class'.

The product was submitted for full scope environmental testing on this basis.

4. It was decided to take T1422 forward for stability and coreflood testing.

2.3.2 Development of Improved 'Bridging' Polymer

Based on our experiences with polyamino acids and on the literature reviews we decided to focus on DADMAC diallyldimethyl ammonium chloride which had been studied previously. Research had already noted DADMAC being used as a clay stabiliser and had indicated its use in bridging. Reference US Patents US 5, 181, 567 and US 5, 038,861. We decided to synthesise increasing orders of molecular weight poly DADMAC using initially homopolymer only, to simplify the chemistry, focussing on higher than 50 K Mw to avoid the patent noted above (<50 K molecular weight), see Figure 2.12 below.

It was designed to leverage on the theory⁵² that the adsorption properties were largely based on changes to the boundary layer by the charge on the "additive".

It was thought that the more positive the charge the greater the affinity for the rock surfaces and the better retention properties offered to the negatively charged scale inhibitor subsequently added. The strong positive charge, under low pH particularly that expected of amine N⁺ based chemistry, was an alternative attractive feature of the DADMAC molecule.

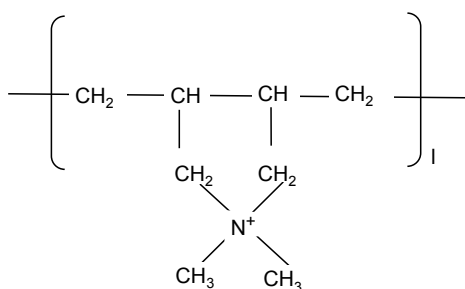


Figure 2.12 : Structure of Poly DADMAC

A molecular weight range of poly DADMAC samples was made by our laboratory team.

Due largely to the limited number of samples of core plugs, of which the damaged plugs only were crushed to provide the basic "crushed core adsorption" material, it was decided to include the best of the new polymer T1422 ie reacted DADMAC and acrylic acid product from the scale dynamic tests in the adsorption tests. A quick adsorption screening run as below using DADMAC Mw 600 K molecular weight was designed.

Adsorption/Precipitation Beaker Tests

The core material was crushed and sieved to less than 2 mm in size, then dried. It was then transferred into 100 ml jars. The adsorption test was carried out as follows:

1. A solution of additive (10% wt) in NaCl brine was prepared and two solutions of scale inhibitor (10,000 ppm by weight) in NaCl brine were prepared.
2. The pH of the additive solution was adjusted to 3 and the pHs of the inhibitor solutions were adjusted to 3 and 5 respectively
3. Additive solution (32 ml) was added to each jar containing crushed core material and the jars were heated to 85°C
4. After 5 hours, 25 ml of each of the supernatants were replaced with scale inhibitor solutions
5. After 24 hours, the contents of the jars were visually inspected and the inhibitor concentration in the supernatants analysed.

The test was also repeated without the step of adding additive solution. In this test, 6% NaCl brine adjusted to pH 3 was added in step 2.

The results are shown in Table 2.3 below.

	Visual Observation	Retention at pH 3 (mg/g)	Retention at pH 5 (mg/g)
6% NaCl brine	AT pH 3 and 5 – clear	3.93	3.85
10% Additive	AT pH 5 – clear At pH 3 – cloudy	7.61	5.04

Table 2.3 : Inhibitor retention level comparison

The results show that retention on the rock surface was significantly increased in the presence of the additive, especially at pH 3. The observation of cloudiness in the supernatant of the jar containing 10% additive at pH 3 suggests that precipitation between the additive and the scale inhibitor occurred.

It was seen that improved retention performance was achieved. It was then decided to screen a range of Mw of the same homopolymer based poly DADMAC⁵².

Effect of Additive Molecular Weight and Scale Inhibitor pH on Inhibitor Retention

The additives used were homopolymers of DADMAC having molecular weights of about 50,000, 500,000 and 1,000,000.

Adsorption Beaker Tests

The core material was crushed and sieved to less than 2 mm in size, then dried. It was then transferred into 100 ml jars. The adsorption tests were carried out as follows:

1. Six solutions (10 %wt) of additives in NaCl brine were prepared. The additives had molecular weights of 50,000, 500,000 or 1,000,000 as shown in Table 3 below. Two solutions of scale inhibitor (10,000 ppm by weight) in NaCl brine were also prepared.
2. The pH of the additive solutions was adjusted to 3 and the pH of the inhibitor solutions were adjusted to 3 and 5 respectively.
3. Additive solution (32 ml) was added to each jar containing sand and the jars were heated to 85°C.
4. After 5 hours, 25 ml of each of the supernatants were replaced with scale inhibitor solutions.
5. After 24 hours, the contents of the jars were visually inspected and the inhibitor concentration in the supernatants analysed.
6. The test was also repeated without the step of adding additive solution. In this test 6% NaCl brine adjusted to pH 3 was added in Step 2.
7. The results are shown in Table 2.4 below.

	Retention (mg/g) Inhibitor solution pH at 5	Retention (mg/g) Inhibitor solution pH at 3
6% NaCl brine	2.64	-
10% Additive 1,000,000 MW pH at 3	6.60	9.77
10% Additive 500,000 MW, pH at 3	7.84	8.96
10% Additive 50, 000 MW, pH at 3	6.19	6.44

Table 2.4 : Inhibitor retention level vs molecular weight

The results show the scale inhibitor retention on the rock surface was significantly increased in the presence of the additive, especially when the inhibitor was used at pH 3. Table 2.4 also shows the retention of scale inhibitor generally increases with increasing molecular weight of the additive. This effect is strongest when the pH of scale inhibitor solution was adjusted to 3.

Cloudiness Figure 2.13 (image B) was also observed in the supernatant phase of the jars containing both additive and inhibitor at pH 3 which suggests that precipitation between the additive and the scale inhibitor occurred.

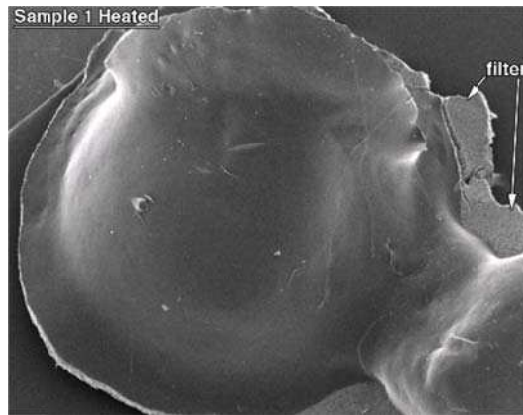
SPE 100466, Fig 1, Ref 4 SEM in paper clearly shows the surface precipitates between inhibitor and additive on the rocks surface.

This clearly explains the step change in expected adsorption and ultimate squeeze life.

It was noted during the compatibility testing that the new additive with the new scale inhibitor under pH 3 and given temperature, brine and concentration formed a white gel like precipitate. The precipitates could dissolve with changing pH, concentrations and temperature. Further investigation indicated the dissolving process could be by hydrolysis in which the two polymers dissociated. If this process is indeed a surface precipitation of the rock/additive then enhanced adsorption/squeeze life would be expected. Unlike conventional Ca^{++} or metal ion precipitations this polymer reaction can be done in two stages avoiding the bulk precipitations and subsequent damage often caused by Ca^{++} /inhibitor precipitation squeeze technology⁶⁷.



Figure 2.13 : Adsorption beaker test (10% inhibitor mixed with 10% additive)



SPE 100466, Figure 1, SEM of precipitated inhibitor with additive.

Core Flood Tests

Based on the beaker adsorption tests it was decided to test the new copolymer and the best molecular weight DADMAC in a full coreflood test.

To maximise the adsorption coupled with precipitation we designed the tests at pH 3.

Coreflood Testing is designed to assess:

- i) if treatment will induce formation damage
- ii) the adsorption of Scale Inhibitor (indication of length of treatment)

The tests are performed with reservoir core, oil and brines under reservoir conditions

It takes up to 2- 4 weeks a test



tus⁵⁴

Coreflood Apparatus

Main Components consist of:

- Inlet Section - fluid reservoirs and pumps
- Core holder and confining system
- Oven (heating coils and core holder)
- Outlet Section - fraction collector & PRVs
- Transducers and data acquisition



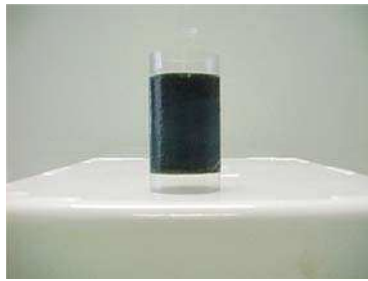
Figure 2.15 : Inside the oven showing the core holder and various mixing heating coils⁵⁴



Figure 2.16 : Automatic sample collector⁵⁴



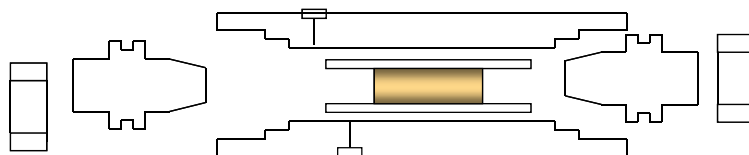
"Core"



Crude oil sample



Core with sleeve prior to inserting in holder



Dismantled core holder



Core inside "holder"

Figure 2.17 : Components of core holder⁵⁴

Coreflood Testing

What you need before you start:

- Field core - representative of formation that will be treated - preserved
- Field temperature
- Field crude oil (water removed)
- Synthetic brine (water chemistry of formation water / pH)
- Which chemical you want to test

Procedure: is specific to test, but generally designed as follows:

- Core is saturated with crude oil / water
- **Permeability** to oil / water measured – **before treatment**
- **Chemical treatment** is effected
- The core is saturated with crude oil / water
- **Permeability** to oil / water measured – **after treatment**
- **Postflush** with synthetic brine – samples collected and analysed for residual chemical
- **Final Permeability** to oil / water measured

Note:

Permeability: is a measure of the ability of a material (eg rocks) to transmit fluids and is measured in Darcy (D).

$$Q = k \cdot \frac{\Delta P \cdot A}{\mu \cdot L} + c$$

cc/sec

C = atmospheres zero shift
K = Darcy

Coreflood Test Procedure

The coreflood test was designed to evaluate the inhibitor return profiles and whether any damage may be caused to the formation. The coreflood procedure was carried out as follows.

1. Injection of formation brine
2. Overnight crude saturation and heat up to 98°C (this temperature was maintained throughout the test)
3. Pre-treatment permeability measurement to crude oil (in forward flow, FF and reverse flow, RF)
4. Pre-treatment brine saturation

5. Pre-treatment brine permeability measurement in FF and RF directions
6. Formation water injection in RF direction
7. Preflush injection (5 pore volumes of 10% additive in NaCl brine) in RF direction
8. Shut in for 5 hours
9. Injection of inhibitor (10 pore volumes of 5% inhibitor in 6% NaCl brine at pH 3) in RF direction
10. Shut in overnight
11. Oil injection and permeability measurement to crude oil in FF and RF directions
12. Formation brine injection at FF direction for 5 days and samples collected for chemical analysis
13. Brine permeability measurement in FF and RF directions
14. Post treatment crude saturation
15. Post treatment crude permeability measurement in FF and RF directions.

The test was also repeated without the step of adding additive solution. In this test, 5 pore volumes of NaCl brine was added in step 7 and a 10% inhibitor solution in 6% Na Cl at pH 3 was used in step 9.

The details are shown in the paper SPE 100466.

It should be noted the inhibitor was added at 5% concentration together with additive. Whereas the test run with no additive had 10% concentration of inhibitor. This was planned to determine the possible savings in inhibitor deployment when additive was used in field treatments.

Results

The inhibitor return profile SPE 100466, Figure 4 (demonstrates adsorption/desorption) shows >30 ppm of chemical after 500 pore volumes of post flush. This clearly demonstrates the positive effect of the "additive DADMAC". This is very strong indication of long squeeze life for a polymer!

Figure 4 also shows the inhibitor at 5% concentration with additive gave better return profile than 10% inhibitor with no additive.

Equally important SPE 100466, Table 4 indicates oil permeability recovery was 93% at 907 mD indicating no 'damage'. No well damage/permeability impairment would be expected based on the SPE 100466, Figure 5 stable differential pressure plots recorded.

Field Treatments

Several successful field treatments were carried out, details in paper, using the newly developed DADMAC additive and the new acrylate DADMAC copolymer. SPE 100466, Table 6 shows the improved squeeze life vs a standard phosphonate.

Note: the rock was sandstone and classed as 'clean' with little or no clays present to aid adsorption. SPE 100466, Figures 6,7,8 demonstrate the improved lifetime. Squeeze life in excess of 6 months obtained resulting in production of 160,000 m³ produced water with no loss in oil production.

Conclusion

The development programme has produced a novel scale inhibitor which inhibits serious barium sulphate scale at low treat rates.

The copolymer exhibits a good retention on sandstone core with boosted adsorption when used with the new poly DADMAC bridging agent. The increased adsorption is further boosted by the reversible precipitation between the bridging agent and the copolymer.

The copolymer can be detected using 'ICP' accurately measuring the 'P' phosphorus which is bonded to the polymer molecule.

Field deployment has proven the products and package are a viable and leading edge/best in class treatment for the applications described in the paper. No reservoir damage has occurred due to the treatments. This package is used in both the UK and Norwegian sectors of the North Sea oil industry.

The package is classified as 'yellow' by the Norwegian authorities indicating excellent properties.

The package is fully commercialised and in use by the oil industry.

2.4 PAPER 3 SPE 113926

"Development of a New Polymer Chemistry for Downhole Squeeze Applications" SPE 113926, SPE Production Operations Journal Vol 24 No.3, August 2009, PCT/GB2006/002877

Scale inhibitor squeeze treatments have regularly been conducted to prevent both sulphate and carbonate scale depositions in a specific North Sea field for more than 10 years. However, some wells, in which the fluid is produced from the "clean" sandstone formation, have experienced relatively

short squeeze lives, when squeezing a conventional phosphonate scale inhibitor treatment. A research programme has been conducted to develop a novel polymer scale inhibitor chemistry, which combines performance in a number of laboratory static and dynamic tests, with improved scale inhibitor adsorption properties on "clean" sandstone formations. Field trials have also been conducted with satisfactory results.

This paper outlines the concept of how novel copolymer scale inhibitor chemistry was developed by incorporating a special monomer. The monomer was introduced to enhance the inhibitor adsorption properties, because it carries a special functional group to improve the scale inhibitor affinity for the reservoir rock. This special functional group plays a key role for the newly developed scale inhibitor, giving improved and acceptable squeeze life. A critical aspect of the programme included optimizing the monomer content to achieve a good adsorption/desorption balance, to ensure that the scale inhibitor would be desorbed/released from the reservoir rock to meet the requirements of an acceptable squeeze programme. An added bonus was that the environmental properties of the scale inhibitor polymer were also improved because of the introduction of the special monomer. A number of beaker and dynamic loop tests were conducted and the inhibitor showed excellent efficiency in both sulphate and carbonate scale inhibition performance tests under the test conditions adopted.

This paper also presents detailed laboratory and field data; the squeeze treatment design strategy and deployment method adopted for the scale inhibitor.

Following the successful performance of the new copolymer scale inhibitor and the homopolymer derived poly DADMAC discussed in SPE 100466, it was decided to further explore both the molecular weight and the completeness of polymerisation reaction of the scale inhibitor manufacture. A full series of environmental/toxicity tests would also be conducted by an GLP approved laboratory. Ideally we would achieve an improved environmental profile but retain the performance characteristics discussed in SPE 100466. The chosen newly manufactured polymer would then be deployed in the field and performance noted. Statoil Hydro encouraged the project.

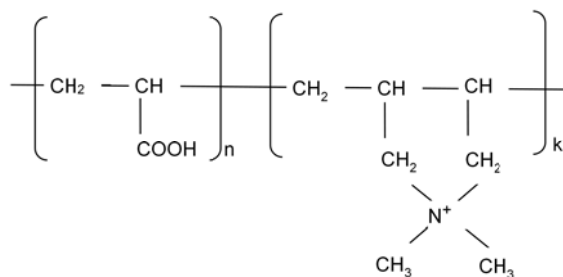


Figure 2.18 : Structure of polyacrylic acid and poly DADMAC copolymer.

Molecules were synthesised and their properties studied over increasing molecular weights (2 K, 3 K, 5 K, 10 K).

The samples were subjected to NMR and GCMS analysis in order to understand how much if any free monomer remained and how the phosphorous which is needed for analytical reasons (ICP) was bound to the molecule.

The decoupled NMR spectrum analysis indicated the P bonding was as C-O-P and in the form of a phosphate ester. We aimed for <1% of the phosphate species to be unbound to a carbon and for greater than 90% of the phosphate to be present as an ester of the large polymeric species.

The synthesis were run with varying times, temperature, ratios of reactants etc to achieve the product with least free monomer at Mw of 3500 and the 'P' attached as ester to the polymer Product "B".

Nuclear Magnetic Resonance

140 μL of sample was dissolved up in 560 μL of D_2O . A broadband decoupled ^{13}C NMR spectrum was acquired referenced externally to the D_2O lock frequency. The probe was tuned to ^{31}P , and the zero point was set to 85% H_3PO_4 . The spectrum was acquired using broadband decoupling.

Analysis of the Spectra

^{13}C NMR The spectrum has been annotated and provided. It clearly shows the presence of low molecular weight (monomers and small oligomers) and high molecular weight (polymeric) species in the form of narrow and broad lines respectively. It appears there are 4 different carboxylate environments in the polymeric species (175-185 ppm) and 3 different monomeric carboxylate species. Remaining monomer double bonds from both monomer species are apparent at 124-136 ppm. At around 60 ppm, the monomeric and polymeric CH_2N peaks are visible, and the NMe peak is present

at 45 ppm, with the remaining aliphatic carbons appearing below this point. The complexity of the spectrum coupled with the broadness of the lines makes it impossible to see any ^{13}C - ^{31}P coupling which would have assisted the identification of the mode of bonding of the phosphate to the polymer.

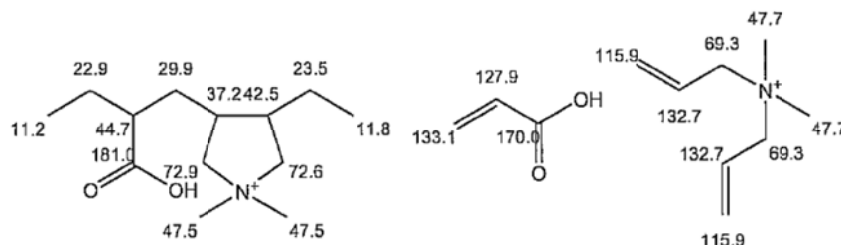


Figure 2.19 : Predicted ^{13}C NMR Chemical shifts for monomer units and part of the polymer.

^{31}P NMR The spectrum has been annotated and provided. It clearly shows two regions – 50-20 ppm containing phosphate ester species and 20-0 ppm containing free phosphate species. Again, there are narrow and broad lines, indicating low molecular weight (monomers and small oligomers) and high molecular weight (polymeric) species, but these mainly occur in the phosphate ester region as expected. It is immediately evident that the mode of bonding of the phosphate species to the polymer is as phosphate esters containing a C-O-P bond. Integration of the areas underneath the peaks for both regions indicates that **3-5% of the phosphate species are not bound to carbon** (ie in the region between 20-0 ppm). The question of how much of the bound phosphate was present as phosphate esters of polymeric, oligomeric and monomeric species required more sophisticated data analysis. For this, separate peaks were integrated and the integrals exported to Microsoft Excel. The monomer/oligomer to polymer cut-off for peak width was put at 30 Hz, with peaks below this width deemed to be monomeric or small oligomers and peaks above this width deemed to be polymeric. From these calculations, it appears that roughly **74-79% of the phosphate is present as phosphate esters of large polymeric species.**

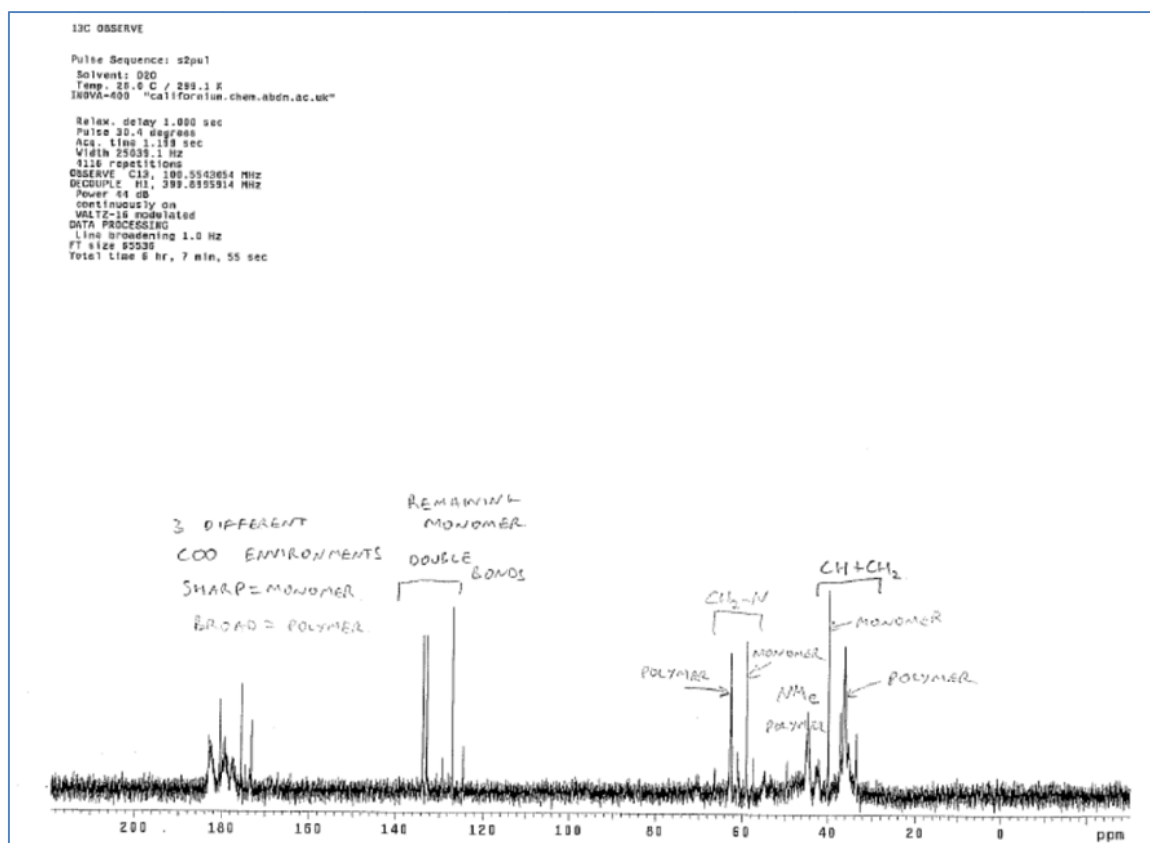


Figure 2.20 : ^{13}C NMR Spectrum of DADMAC acrylate copolymer

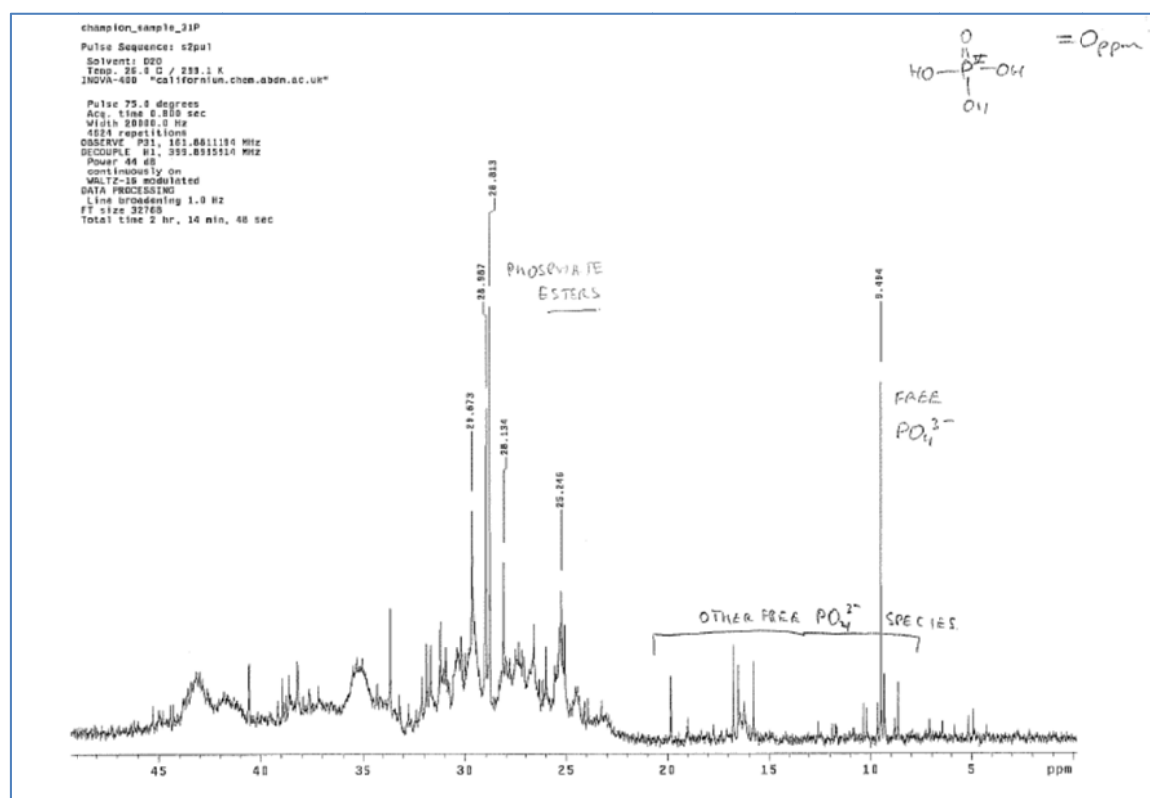


Figure 2.21 : ^{31}P NMR Spectrum DADMAC acrylate copolymer

Some early NMR scans are attached for information only.

Many examples of scale inhibitor including polyacrylates, copolymer of acrylate and sulphonate polyaspartate³³ and capped polymer^{34,35} and PMPA³⁶ have been synthesised and tested/deployed in the oilfield. However for specific circumstances there is a need to develop new chemistries. The drivers are oil companies who are producing from more difficult fields with higher pressures and temperatures with difficult connate waters and governments who are demanding greener, purer chemistries are used. Focus is on low toxicity, low bioaccumulation and over 60% biodegradation achieved in industry tests run by GLP Laboratories. The accuracy of analysis methods and molecules containing 'tags' to facilitate analysis are under constant review. Finding <3 ppm \pm 1 ppm of a polymer in oilfield brines is a real achievement. For this reason our interest in binding sufficient levels of phosphorus "P" tag onto the polymer is obvious.

A copolymer of DADMAC acrylic acid named Product "B" was synthesised and selected for the following test programme.

Experimental

Details of Dynamic Scale Loop and Compatibility Tests in Paper SPE 113926 and also earlier in Paper 2.

Results

- A treat rate at 5 ppm inhibited scale for over 3 hours. This is high end performance in this type of test and qualified product B as a suitable scale inhibitor for this water chemistry
- Compatibility Tests – SPE 113926, Table 2 synthetic water used and product B dosed at 10, 15, 100, 1000 ppm and 1%, 5%, 10%, strength. Temperature set 98°C. Product B fully compatible – based on visual clear solutions after 24 hours. Product qualified for core test on this stability in brines basis.



Figure 2.22 : Scale inhibitor brine compatibility tests



Figure 2.23 : Scale inhibitor diesel compatibility tests

- Corefloods – Preflush ‘additive’ was included in one of the two tests with product B. The ‘additive’ was selected based on its performance detailed in^{37,38,39}. Core test run as per design in paper SPE 113926 and methodology detailed in Paper SPE 100466.

Results of Coreflood

As shown in SPE 113926, Table 3 **Flood 1** Oil Permeability at 98°C was 1324 md in forward and 998 md in reverse. After product B was injected flowback was 954 md forward and 841 md in reverse.

Flood 2 - 70% and 100% of oil permeability recovered after injection of product A and product B in forward and reverse directions respectively, ie 837 md in forward and 1034 md in reverse. This is better return permeability than Flood 1. It appears Product A/B combination may enhance oil permeability recovery.

SPE 113926, Figures 4 and 5 indicate no pressure change during the corefloods. Products have not damaged the cores or caused injectivity issues.

SPE 113926, Figure 6 indicates the inhibitor "B" return profile during the corefloods with and without preflush product "A". The data is generated by sampling the return fluids on regular basis and subsection to ICP analysis for 'P' phosphorus vs a standard solution of the inhibitor. The method is well documented and accurate to ± 1 ppm at down to 3 ppm product B.

The results show preflush treatment gives >10 ppm for over 800 pore volumes against 5 ppm at the 500 PV Stage when no bridging agent present in the preflush.

This indicates an acceptable squeeze life would be expected if the package were deployed in the field.

SPE 113926, Table 4 shows a mass balance of the Flood 1 and 2 experiments.

The data indicates lower return percentages of the applied chemicals for the preflush Flood 2 version indicating longer retention/adsorption and likely squeeze life.

SPE 113926, Figure 7 shows the inhibitor "B" return ppm and the 'ion tracking' from a field deployment of Product A preflush and product B. The Ba^{2+} remains high subsequent to squeezing indicating ongoing scale inhibition and presence of inhibitor.

It should be noted Well A formation is referred to as a 'clean' rock with little or no clays which would indicate poor adsorption likely with polymers or phosphonates.

It can be seen the inhibitor "B" return remains above the MIC on 08/08/07 which is over 5 months and 112,500 m³ of produced water. No loss of well productivity is noted and the Ba level indicates no sulphate scaling is yet recurring.

Environmental Test Results

SPE 113926, Table 1 the toxicity testing results from GLP approved environmental laboratory are shown. Product "B" the copolymer, has an excellent profile and is regarded as "yellow" by the Norwegian Authorities.

It is thought the introduction of more double bonds to the molecule has increased the sources where biodegradation occurs. This increased biodegradation possibly improves the toxicity performance over the longer test period.

Conclusion

- A highly biodegradable co-polymer inhibitor containing acrylate and quaternary amine DADMAC has been developed.
- Laboratory tests designed to assess compatibility and product performance at the field conditions showed that the scale inhibitor in combination with a preflush agent may offer an acceptable solution. The MIC of this inhibitor was measured at 5 ppm at the laboratory test conditions and the loop tests were conducted at 50:50 of seawater and formation brine, representing the highest scaling potential.
- In the core test program, two reservoir conditioned core floods were performed. The first core flood was carried out using scale inhibitor only. The second core flood was performed with pre-flush additive and followed by scale inhibitor. Both core floods showed an acceptable level of return oil permeability and good inhibitor returns. A longer inhibitor return was seen from the second core flood with the pre-flush additive than that of the first core flood without using pre-flush additive.
- In order to demonstrate the effect, of the enhanced inhibitor return on the application of preflush additive, further the simulation was carried out using Squeeze VI to simulate the inhibitor returns for both corefloods with and without using the preflush additive. Good inhibitor return data matches were achieved for both core floods and a longer inhibitor return was again demonstrated from the coreflood returns when using the preflush additive, ie longer treatment life indicated.
- The field trials performed to date have not encountered any significant pressure build up during injection and good post treatment PI has been achieved.
- Inhibitor returns over ten months after the treatments remain significantly above MIC, indicating the potential for long treatment life with the new scale inhibitor.

A new product "B" was developed and satisfactorily trialled. The product has now been used in over 30 field applications with excellent protection life and no well damage.

Product "B" has an excellent toxicity profile and is classed as "yellow" by Norway. Subsequent to the published paper product "B" has been the subject of an extended analytical development programme incorporating concentration step ups using Sep Pak cartridges on the samples prior to the ICP analysis. We can now detect product B down to 2 ppm in oilfield produced brines.

To date for the conditions specified the new copolymer is the product of choice for these fields scale control. Production with no scale forming has saved millions of dollars on the one oilfield alone.

2.5 PAPER 4 SPE 135249

"Meeting the Challenges in the Down-hole Scale Control for High-Water-Production Horizontal Wells in an Environmental Sensitive Part of the Norwegian North Sea." SPE 135249 Journal of production and Operations 21 Dec 2011. PCT/GB2007/600099

The work described in this paper is a continuation of the polymer scale inhibitor development work which started initially with polyaspartates and the subsequent synthesis of an acrylate DADMAC copolymer through to field trials and adoption for use by multinational oil companies.

At each stage there has been the requirement for improved scale inhibition performance, squeeze life extension and improvements to meet the environmental demands of the Norwegian North Sea authorities.

Product "B"⁴⁴ (Paper 2.3) exhibited good all round performance but the field scaling condition experienced in some high barium produced water wells demanded a more efficient and compatible BaSO₄ scale inhibitor^{40,41}.

Amongst other ideas it was decided to formulate some terpolymers based on the so far successful idea of reacting monomer with DADMAC to leverage on the adsorption biodegradability and low toxicity of the DADMAC molecule.

We presumed inclusion of the DADMAC or amine polymer would ensure good adsorption at low pH and desorption at the higher pH of produced water systems. The low pH 'protonated' scale inhibitor would exhibit the electrostatic properties enhanced by hydrogen bonding and Van der Waal's forces of attraction^{42,43}.

Inhibitor development

The series of terpolymers were synthesised including the molecules below.

1. A terpolymer from fumaric acid, acrylic acid and diallyl dimethyl ammonium chloride (DADMAC)
2. A terpolymer from maleic acid, acrylic acid and DADMAC.

Both chemicals are random polymers and their structures are as Figures 2.24 and 2.25 below.

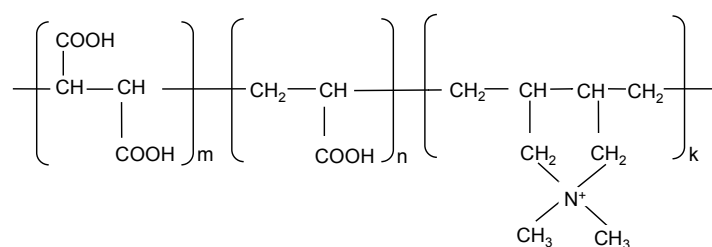


Figure 2.24 : Structure of terpolymer containing fumaric acid, acrylic acid and diallyldimethyl ammonium chloride

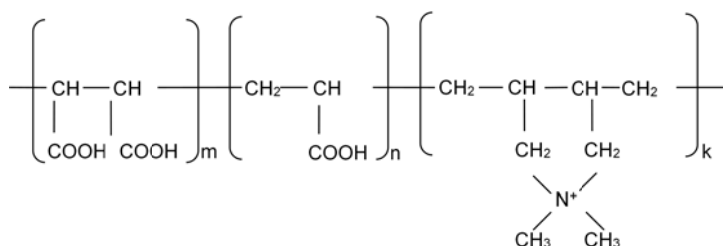


Figure 2.25 : Structure of terpolymer containing maleic acid, acrylic acid and diallyldimethyl ammonium chloride

Broadly speaking, the molecular weight of both polymers can be ranged from 800 to 50,000⁵². The mole ratios of m:n:k can be from 1:1:1 but preferred ratios should be 1: (1-100):1 or (1-20):(1-100):(1-20). Some inorganic groups, such as SO_4^- , SO_3^- , HPO_3^- and HPO_4^- from initiators, can be connected with COOH groups to tag the inhibitor. In other way, these inorganic groups can be connected at the ends of the monomer of polyacrylate CH_2 - chain. Once terpolymers are tagged with HPO_3^- and HPO_4^- , the chemical can then be easily measured using ICP.

The terpolymers of fumaric acid, acrylic acid and DADMAC and maleic acid, acrylic acid and DADMAC were prepared in a reactor equipped with a mechanical stirrer, a reflux condenser, a thermometer and inlets.

Reactants

Acrylic acid

Fumaric acid or Maleic acid

DADMAC (60% in water)

Sodium hypophosphite

Sodium persulfate

NaOH

Deionised water was added to the reactor and heated to 60°C. The monomers (ie acrylic acid fumaric acid or maleic acid and DADMAC) were then added and the solution stirred. NaOH was added to neutralise the reaction mixture and the initiator (sodium persulfate) and chain transfer agent (sodium hypophosphite) were added to induce polymerisation. The reaction mixture was then allowed to reflux and stir for 2 hours. The resulting terpolymer was then cooled.

Experimental Details

In order to evaluate the performance of the above chemicals, in controlling scale deposition, dynamic loop tests were conducted.

The brines used in this study were synthetic Heidrun formation water and seawater made from dissolved salts with the composition given in Table 2.5.

Composition mg/l	Heidrun Formation Water	Sea water
Na ⁺	19510	11150
K ⁺	545	420
Ca ²⁺	1020	428
Mg ²⁺	265	1410
Ba ²⁺	255	0
Sr ²⁺	145	0
SO ₄ ²⁻	0	2800
Cl ⁻	33190	20310

Table 2.5 : Water Chemistry Used in the Tests

Dynamic Loop Tests:

The dynamic scale inhibitor performance test was designed to evaluate the ability of the test inhibitor to delay the nucleation and growth of scale on a pre-scaled metal surface. All tests were performed

with mixed brined at 50:50 formation water and seawater (see Table 2.5). The test conditions were designed to represent the worst case of barium sulphate scaling conditions at the temperature of 90°C.

The method and apparatus have been described in previous papers.

Experimental Results

Dynamic Loop Results for Fumaric Terpolymer

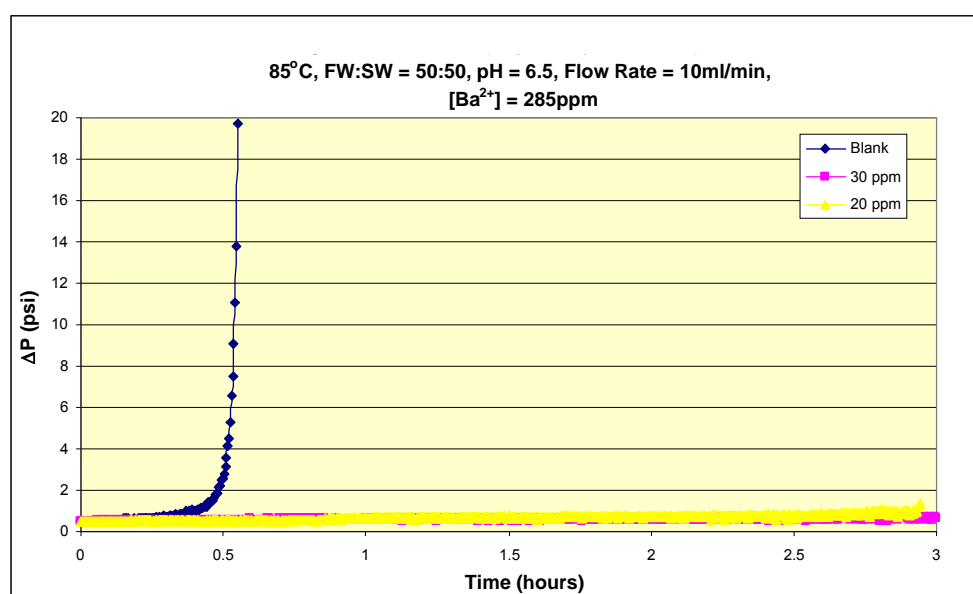


Figure 2.26 : Fumaric terpolymer dynamic loop tests

Figure 2.26 above presents the experimental loop results from the dynamic loop tests using the fumaric terpolymer. The plots show the differential pressure measured vs. the time. The blue line represents the test without scale inhibitor (the blank) where the scale was quickly built up inside the coil, resulting in a steep increase at 0.5 hours of the differential pressures. The pink and yellow lines represent the tests which had 30 and 20 ppm of scale inhibitor in the mixed brine. The differential pressure increase was delayed due to the presence of scale inhibitor. Both pink and yellow lines clearly show that when inhibitor concentrations were dosed at 30 and 20 ppm, the barium sulphate scale precipitation was well controlled, resulting in stable differential pressure readings.

Figure 2.27 presents the experimental loop results from the dynamic loop tests using maleic terpolymer. The plots show the differential pressure measured vs. the time. The red line represents

the test without scale inhibitor where the scale was quickly built up inside the coil, resulting in a steep increase of the differential pressures. The blue line represents the tests with 40 ppm of scale inhibitor in the mixed brine. The differential pressure increase was delayed due to the presence of scale inhibitor. The dynamic loop result clearly shows that when inhibitor concentration was dosed at 40 ppm, the barium sulphate scale precipitation was well controlled, resulting a stable differential pressure readings.

In summary, the dynamic loop tests demonstrated that both new terpolymers were good scale inhibitors. Under the given conditions where the barium concentration is as high as 285 ppm, the scale inhibitor can control the barium sulphate precipitation in the dynamic loop at 20 - 40 ppm for 3 hours test duration.

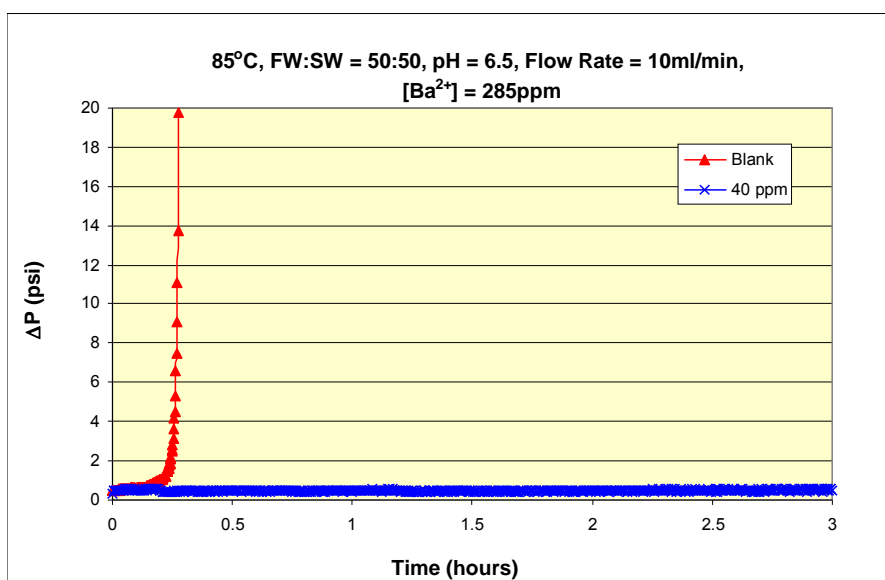


Figure 2.27 : Maleic Terpolymer dynamic loop tests

- i) Terpolymer containing fumaric acid, acrylic acid and diallyldimethyl ammonium chloride has been developed as a scale inhibitor.
- ii) Terpolymer containing maleic acid, acrylic acid and diallyldimethyl ammonium chloride has also been developed as a scale inhibitor.
- iii) The dynamic loop test results demonstrated that fumaric terpolymer is superior to the maleic terpolymer in dynamic tests. It inhibits barium sulphate scale at the concentration as low as 20 ppm (parts per million) under the North Sea reservoir conditions where barium concentration is as high as 285 ppm.

The fumaric/acrylic/DADMAC newly developed product was selected based on this BaSO₄ inhibition performance laboratory testing. This terpolymer was then screened vs updated field information for:

- Brine compatibility
- Inhibitor efficiency
- Corefloods (a) Terpolymers dosed as a water based inhibitor (b) Terpolymer dosed in a gel package^{2,3,4,8,41}.

Note: When the project reached this stage the field produced water chemistry was found to have changed to a barium level of only 94 mg/l. The new water chemistry was used in the subsequent tests SPE 135249, Table 1.

The test techniques have been detailed in earlier discussions.

Results

- The product was found compatible in all ranges of concentration in formation water at temperatures up to 95°C. SPE 135249, Figure 2
- Scale inhibition efficiency at Ba²⁺ levels of 94 mg/l was found to be 5 ppm. Note – the well chosen had fast SW breakthrough pushing the Ba down from 200 to approximately 100 mg/l. SPE 135249, Figure 3.
- Coreflood showed little permeability or injectivity impairment when water based terpolymer was used. Return curves indicated 10-22 ppm remaining after 500 pv postflush. SPE 135249, Figure 4 indicates good adsorption/desorption.
- The gel packaged⁴¹ inhibitor had adsorption curve around 10-20 ppm up to 200 pv. SPE 135249, Figure 5 which although acceptable is inferior to the water based polymer coreflood.

Field application

The fumaric based product was taken forward for field deployment based on this data.

Well A would be squeezed using the gel package which had been used many times by the oil company.

Well B would be squeezed using the water based terpolymer product alone – no gel!

Note –

1. The wells concerned were long horizontal wells which make it difficult to get even placement along the length when bullheading the fluids. The gel package utilises the effects of shear thickening/thinning to get better distribution along the length of the well.
2. The superior adsorption indicated by the coreflood experiment gave confidence to go for the non gel package. The gel package is expensive and has not a good environmental profile.
3. The coreflood return from the gel experiment was extended to 500 pv to collect data for a complete model Squeeze VI programme. Squeeze VI is extensively used^{9,10} nowadays to predict squeeze life based on data from core floods. The model allows design calculation to be done fast and is combined with an excellent graphics package which prints the curves/data modelled. Many of the elements of a squeeze can be explored using the program which indicates the sensitivity of the elements, eg concentration of chemical, overflush volume, squeeze life, return ppm etc etc. When the actual field squeeze returns are obtained, Squeeze VI is used to model the data and compare the isotherm to that from the coreflood. The new isotherm can then be used to design the next squeeze treatment.

Result

Both squeeze jobs were deployed with no problems encountered

Fast return production and water clean-up experienced

Well A at the time of paper writing had back produced/protected 600,000 m³ water, see Figure 8 in SPE 135249.

Well B squeeze procedure (no gel) had no problems with the deployment and gave a fast return to production with clean produced water experienced. The inhibitor performance at paper writing had protected 150,000 m³ and was yet way above the MIC. Subsequent treatments using this water based terpolymer have lasted over 400,000 m³ produced water flowback.

Squeeze VI based on the core data isotherm indicated the gel squeeze treatment would last 240 days flowing at 4100 m³ water/day and still have ppm above the MIC of 5 ppm.

Conclusion

The challenges with controlling scale in this field were exacerbated by the high water production rate, horizontal wells completion, serious barium sulphate scaling potential coupled with stringent environmental regulations.

The inhibitor would also be required to have a longer squeeze life than commercially available products at that time. This would help offset the massive costs of deploying treatments from an intervention vessel with high day costs.

The combined effect of these challenges encouraged the operating company to work with a chemical service company on a joint R&D programme to develop a chemical inhibitor with improved adsorption/desorption (MIC) minimum inhibitor concentration vs barium sulphate in particular.

Non damaging reservoir deployment was a must have.

The new developed fumaric terpolymer has been used on over 60 well treatments since this reported work.

The treatments have been successful with no well damage. Accurate residual analysis using the 'P' tag on the molecule for ICP and SepPak method has been demonstrated. Acceptable scale control over a range of water chemistry, eg Ba 280 to 78 mg/l with significant SW breakthrough has been achieved together with clean water being back produced – dramatic improvement over conventional available phosphonate and acrylate polymer chemistries. The new molecule meets the legislated environmental restrictions. See SPE 135249, Table 2.

Significant savings through not requiring gel packaged treatments have been achieved. Combined with this, the squeeze life achieved by the new terpolymer has resulted in millions of dollars savings to the operating company.

(Patent PCT/GB2007/000099 granted (Europe, Australia, Canada, US.)

2.6 PAPER 5 SPE 50706

"Development of an Oil Soluble Scale Inhibitor for a Subsea Satellite Field" SPE 50706

SPE JPT March 1999. US Patent US6,379,612 B1 April 30, 2002

The formation of oilfield scales is often caused by the mixing of incompatible waters and/or by changing pressure and temperature causing a reduction in the solubility of the dissolved salts in the produced water. To inhibit scale formation a chemical inhibitor typically operates by either nucleation

inhibition or crystal growth modification. Almost all scale inhibitor chemicals are water soluble and are typically deployed continuously by injection or by squeeze from an aqueous phase. In most circumstances water is the preferred carrier medium since it allows instantaneous mixing and rapid interaction with the scaling ions. However, for treating a water sensitive formation or a well with poor lifting energy, the application of a conventional water based scale inhibitor squeeze may have many drawbacks.

These include extended clean up period, increased water saturation in the near wellbore area, cessation of production due to water ingress. Either of these can result in significant loss or deferment in the oil production. In this paper a new range of scale inhibitors which are solubilised in the hydrocarbon phase are described. These new oil soluble scale inhibitors offer some advantages over the conventional water based products. Furthermore, unlike the oil 'miscible' products of the past, these new scale inhibitors do not contain any mutual solvent which sometimes can cause process upset during the backflow after the squeeze treatment. The paper will focus on the development of a product which is specifically designed for a sub-sea satellite field. Due to its unique properties some of the standard test methods and selection processes had to be modified.

Special considerations on the treatment design are also needed due to any deployment constraints in the field, eg vertical wells or long horizontal wells.

Historically scale control in producing oilwells has been effected by bullheading water based scale inhibitors down the well and radially out into the reservoir formation. The inhibitor is chosen after many laboratory based performance tests including adsorption-desorption characteristics and having a desirable isotherm as described in many papers including^{49,50,51}. However, numerous wells have exhibited damage associated with the water based scale inhibitor packages squeezed, which resulted in permanent loss of production and serious workover costs to restore productivity^{45,47}.

In early life many oilwells are referred to as 'dry' and produce very small amounts of connate water. Depending on the confidence in reservoir simulation, prediction of seawater breakthrough, and the likely increasing water production profile ideally wells are treated in advance of predicted serious scaling occurring.

This means introducing hundreds if not thousands of barrels of water in the scale squeeze package into the 'dry' largely oil wet producing area of the reservoir and the near wellbore perforations. Experience has ranged from loss in oil production on backflowing the well to significant increased

pressure as the squeeze was being initially pumped into the well. One of the reasons is the change in permeability of the oil zones when water is forced in, resulting in change of oil wet to water wet characteristics.

The now water-wet rock presents a 'barrier' to oil flow which does not then recover^{45,46,47}. Water will flow easily over and through oil wet reservoir rock but oil will not easily flow over water saturated rock^{45,47}.

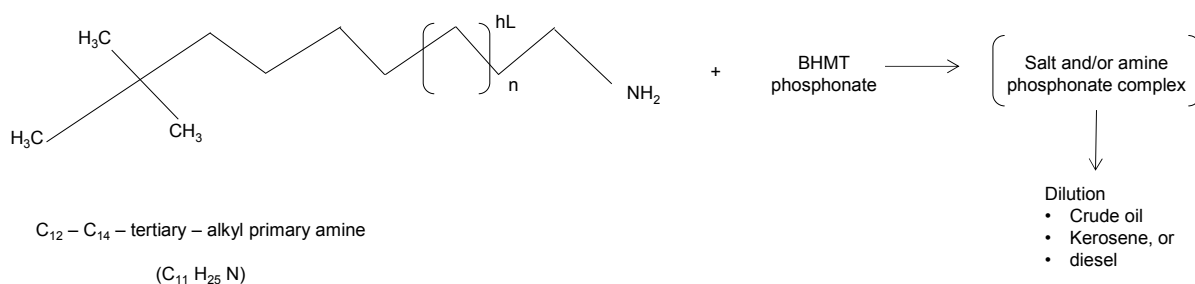
This paper addresses the wettability issues particularly in treating relatively dry wells by describing the deployment of a novel oil soluble scale treatment package which clearly avoids introducing water to the near wellbore with the squeeze package.

Injecting industry standard water based scale squeeze packages will likely in wells with <20% water production increase the water saturation of the formation and thus lower the hydrocarbon relative permeability, causing serious loss of oil production from that zone when the well is brought back on-line. This is an industry rule of thumb.

Many other advantages are to be gained from using 'oil soluble' or OSi scale inhibitors:

- Low density vs water based inhibitor gives better 'lift' to low pressure wells (lower hydrostatic head)
- Pumping long distances through subsea pipelines to the wellheads (up to 20 km away) is improved by the lower density and low viscosity OSi as is return flow
- Wells can be squeeze treated earlier in life because of the unlikely negative rel-perm effects
- Avoidance of water block and or 'coning'.

The OSi products are the subject of a granted patent US 6,379,612 B1 which describes the product chemistry and helps the reader understand OSi.



'Primene' Rohm & Haas

Figure 2.28 : Reaction pathway for OSi formation (US Patent 6379,612. 2002)

It should be noted that only a narrow range of primary amines exhibit the properties which produce the OSi as described. The scale inhibitor component can be phosphonates, eg BHMT or DETA and some polymers have shown promise.

The OSi when exposed to brine will partition into the brine phase. The partition kinetics mass transfer will depend on numerous factors, temperature, brine, hydrocarbon etc, but has been shown to be fast. The OSi then adsorbs by postulated hydrolyses and electrostatic charge to the rock surface, and is then in position ready to desorb into water when it comes into contact. The OSi scale inhibitor component then performs as a normal scale inhibitor of that chemistry.

Figure 2.29 shows the postulated process whereby the OSi in coming into contact with water in the reservoir partitions into the water phase and on hydrolysis leaves the amine and oil components in the oil phase. The free scale inhibitor then adsorbs as expected onto the sand or rock surface.

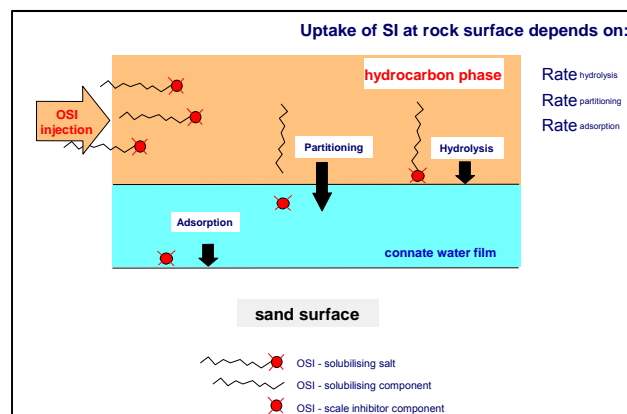


Figure 2.29 : Mass Transfer of OSi molecules from bulk oil phase to rock surface

Figure 2.30 shows the postulated process where the back production of the well causes the oil flow to sweep the amine and oil components out of the reservoir. The adsorbed scale inhibitor awaits produced water to pass over it and will then desorb into the water and return to the wellhead preventing the produced water from scale formation.

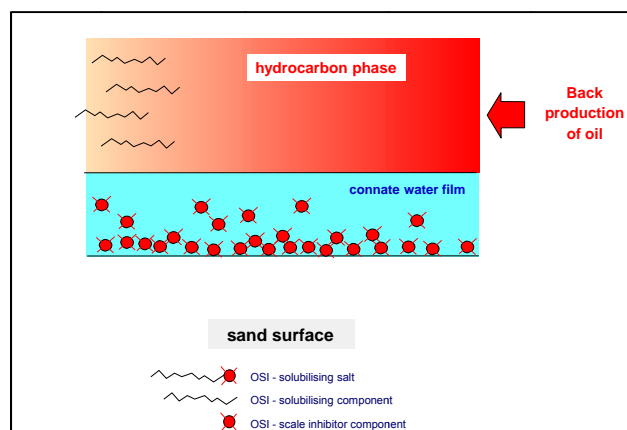


Figure 2.30 : Mass Transfer of OSI molecules from bulk oil phase to rock surface

In the case of a penta phosphonate OSI the OSI partitions from the oil based carrier into the water phase/connate water and hydrolysis takes place. Experiments reported in this paper have shown at temperatures over 70°C the mass transfer and hydrolysis is complete in around 30 minutes.

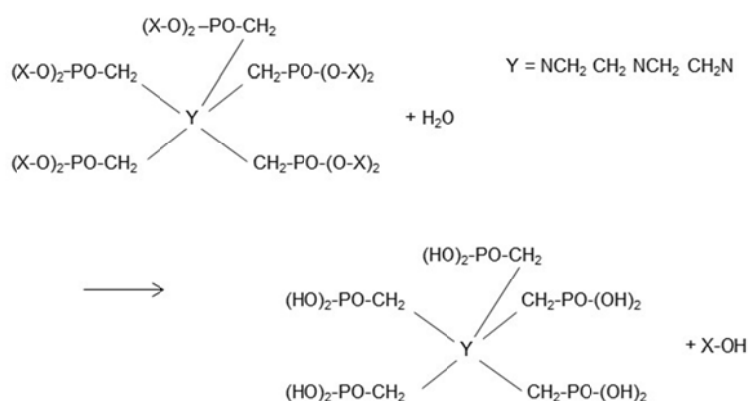


Figure 2.31 : Hydrolysis of a phosphonate

This paper SPE 50706 describes the selection of a suitable solvent carrier and its effect on hydrolysis and partitioning of the OSI, the inhibition performance of the product vs BaSO₄ and finally the coreflood tests results of injectivity, and retention characteristics of the scale inhibitor package. The design was specific to a subsea satellite field.

Experimental

A 10% OSI solution made up in each of crude, kerosene, diesel, paraffin and xylene and each then mixed at 5:1 in formation water. Shaken and temperature set at 80°C overnight. Other than xylene all separated clearly and phosphorus by plasma analysis showed >99% of OSI partitioned to the water

phase. <0.1% remained in the solvent package. It was noted the concentration in the water was approx. x 5 original to the solvent mix.

This enhanced partitioning has big positive implication for efficiency of the field deployment and ultimately life of squeeze.

A similar test was run at 0,20,50,70,90 °C for 4 hours. Again little or no chemical remained in the solvent carrier, indicating low sensitivity of partitioning to temperature and the partitioning mass transfer to water phase is **fast**.

Scale Inhibition Performance Test

The dynamic loop blocking test was utilised. Water chemistry was the targeted field formation water with boosted Ba content to 400 ppm to speed up the testing by focusing on severe barium sulphate conditions and to cope with the worse case.

The OSi was dosed to the seawater and heated to 90°C. The water phase was extracted and on cooling injected to the coil with the formation water. The dose rate was varied to find the MIC. Included were standard water based scale inhibitors including the chemical used in the OSi.

The OSi performed similarly to its water based generic and a commercial sourced sulphonated copolymer.

Adsorption Test

A new technique, to study the effect of adsorption/desorption on a sand column, was implemented. The sand column was placed upstream of the coil in the p-mac TEST, details in paper. Both were submerged in a water bath at 90°C. The column was subjected to:

- Saturation with seawater
- 50 ml kerosene injected to displace the mobile water
- Injected 100 ml, solution of OSi and shut in overnight*
- Injected 50 ml kerosene
- Seawater flowed through column and into premix stage upstream of coil
- Second line upstream coil was flushed with formation water
- Effluent from coil collected

Complete column procedure repeated with step above using 100 ml of the same (activity concentration) generic chemical in water.

Results

1. Indicated good return profile from column which showed the OSi had hydrolysed/adsorbed on the sand and then desorbed. See SPE50706, Table 3, paper below.
2. The OSi based performance was superior to a same generic "blank" water based test indicating again the effect of "enhanced partitioning", ie mass transfer from the OSi giving more chemical to adsorb on the sand and to desorb later.
3. The SPE 50706 Table 3, clearly shows the OSi had a superior adsorption to the sand column protecting the water from scaling for double the time achieved by the water based equivalent same chemistry scale inhibitor.
4. The decision was then made to go forward to the final step of coreflood testing which is more time consuming, higher tech and has limited good quality core plugs available to the test lab.

Coreflood

A standard coreflood test programme was carried out with the OSi and with the generic water based scale inhibitor. The effluents from both the adsorption and the desorption stages were collected and analysed. Procedure as in SPE 50706.

Results

1. No injectivity problems were identified (ΔP remained acceptable) SPE 50706, Figure 6
2. The adsorption/desorption profile was good for 3 ppm after 600 pv, SPE 50706, Figure 5, and
3. Interestingly we observed some mobile water exited near the end of the kerosene overflush. This is a characteristic of OSi and thought to be attributed to the hydrolysis/mass transfer of the OSi changing the interfacial tension in the phase fronts in contact with the connate water.

Finally a series of compatibility tests were run with ratios of 1:9 to 9:1 with OSi pill (10% in kerosene) and synthetic formation water. Only slight haziness seen at 9:1 formation water : OSi. All ratios exhibited complete partition of OSi scale component to the water phase.

Conclusions

1. The paper indicated OSi molecules readily partition and hydrolyse to give excellent adsorption/desorption profiles on sand and core
2. The produced water 'clean up' period is found to be shorter when OSi type chemicals are deployed. This means less problems handling oil water and risking serious fines from the authorities.
3. Mass transfer of OSi from oleic to water phase is fast and appears irreversible
4. Enhanced partitioning is a characteristic of OSi and gives improved chemical utilisation
5. No negative relative permeability effects noted. Again pointing to suitability for "dry" well applications.
6. The mass transfer of OSi from oil to water phase appears to be irreversible. This demonstrates the OSi scale inhibitor component will adsorb on the rock and await water production before it desorbs. This is ideal for treating new 'dry' wells.
7. OSi deployments in low pressure wells can give better faster return to full production as a consequence of the lower density of the squeeze package and its hydrostatic effects.

Note:

The suitability of OSi for "dry" wells and indeed wells/cores which are found to be water sensitive was noted by Statoil who embarked together with Champion Technologies on patenting "Squeeze on Completion" WO 0159255(A1). The idea was to treat wells, found to have high scale potential and where deployment was difficult or expensive – subsea and deep wells, immediately the drilling and clean-up process completed. The OSi would not change the wettability of the rock or the relative permeability and the chemical would be adsorbed and await water breakthrough whenever the water front arrived. This would give warning/action time to the operating company who could then plan a scale prevention strategy before the well was potentially scale damaged.

More than 50 OSi squeezes were deployed over a 5 year period. Some excellent papers were filed. In particular SPE 60197 NJ Jenvey et al "The Application/Oil Soluble Scale Inhibitors into the Texaco Galley Reservoir" Second International Symposium on Oilfield Scale UK January 2000.

Jenvey paper compares a conventional water based squeeze with an OSi deployment in the same field similar wells. The paper highlights the negative effects of changing wettability of "dry" wells by

deploying water based squeeze jobs. It also indicates the lower likelihood of negative oil relative permeability effects with OSi technology.

An ideal coreflood from the Jenvey paper where no ΔP increase or relative permeability damage indicated is shown below, SPE 60197, Figure 7,⁴⁷.

Note the dramatic increase in ΔP with the water based scale inhibitor shown in SPE 60197, Figure 6,⁴⁷.

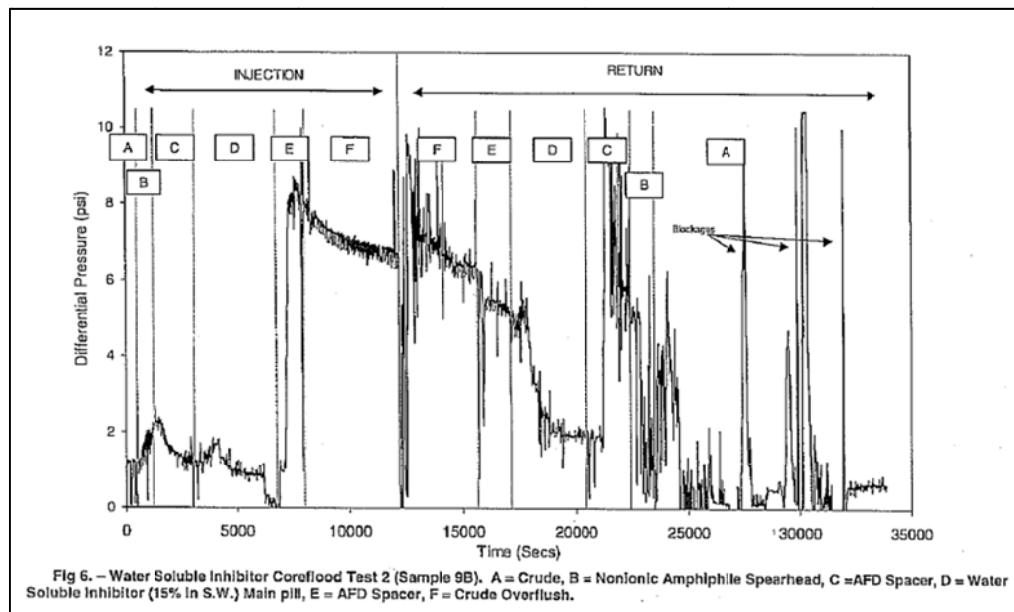


Figure 6 : Coreflood water based - SPE 60197 Jenvey et al, January 2000

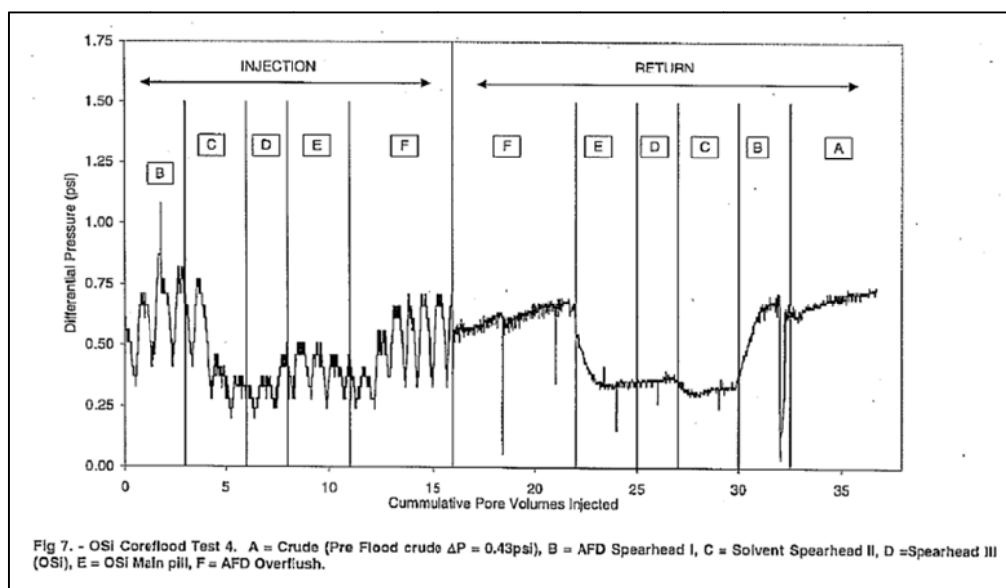


Figure 7 : Coreflood OSi - SPE 60197, Jenvey et al, January 2000

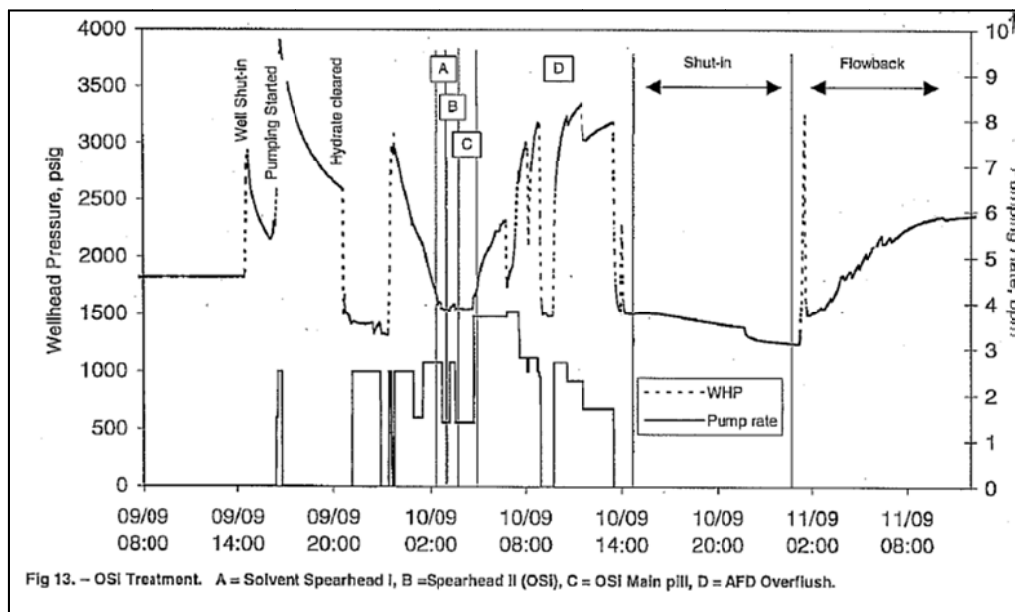


Figure 13 : Field deployment OSi – SPE 60197, Jenvey et al, 2000

The later field deployment mirrored the corefloods with water based squeeze indicating damage to the well whereas the OSi deployment returned the well to full production in a matter of hours⁴⁷. Wellhead pressures are a clear indication of good injections rates and on flowback the pressure was better than before the intervention. Figure 13 SPE 60197 clearly demonstrates the successful field deployment of OSi.

APPENDICES

APPENDIX I - PEER REVIEWED PAPERS

Full print of SPE Papers and SPE production Operations manuscript references (Peer Reviewed)

PAPER 1	SPE 80377	A Way Beyond Scale Inhibitors – Extending Scale Inhibitor Squeeze Life Through Bridging
PAPER 2	SPE 100466	Field Experience in the Application of an Inhibitor/Additive Interaction Package to Extend an Inhibitor Squeeze Life
PAPER 3	SPE 113926	Development of a New Polymer Inhibitor Chemistry for Downhole Squeeze Applications
PAPER 4	SPE 135249	Meeting the Challenges in the Downhole Scale Control of High-Water-Production Horizontal Wells in Environmental Sensitive Part of the Norwegian North Sea
PAPER 5	SPE 50706	Developments of an Oil Soluble Scale Inhibitor for a Subsea Satellite Field

Joint Authorship Declaration



SPE 80377

A Way Beyond Scale Inhibitors – Extending Scale Inhibitor Squeeze Life Through Bridging

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Abstract

The Heidrun Field is located in the Haltenbanken area offshore Mid-Norway. The reservoir temperature is 85–88 °C and the reservoir pressure is close to hydrostatic pressure, around 250 bar. Seawater injection is utilized to increase recovery and for pressure support. With Ba^{2+} levels averaging about 200ppm, downhole sulphate scale deposition caused by seawater injection has been identified. The field came on stream in 1995. Heidrun presents a particular challenging scaling environment due to the combination of high Ba^{2+} content, demand for environmental friendly chemicals, strong top-side emulsion tendency, limited hydrostatics and at times high draw down within the gravel packs. In addition, the high kaolinite content (20–30 %) in the reservoirs introduces the risk of fines mobilization leading to plugging within the gravel packs especially with the development of overflush fluids volumes used during squeeze treatments. Scale control started in November 1999 with regular squeeze treatments. However, initial squeezes suffered from short treatment life and evidence of fines related productivity decline.

Under a joint R&D program, a multi-functional additive was developed that enhanced inhibitor adsorption, provided clay stabilisation and a certain level of scale inhibition.

This paper presents both laboratory and field data to elucidate the mechanisms involved in extending squeeze life and clay fines stabilization with this additive.

Introduction

The Heidrun Field has been described in several papers over the past years^{1,2,3,4,5} and only a short overview is given here. The field is located in the Haltenbanken area offshore Mid-Norway, and was discovered by Conoco in 1985. It has been producing since 1995 with Statoil as operator. License owners are Petoro (64.16 %), ConocoPhillips (18.29 %), Statoil (12.43 %) and Fortum Petroleum (5.12 %).

The hydrocarbons are present in three reservoirs of Jurassic age at depths around 2400 m TVD MSL. The reservoir temperatures are from 85 to 88 °C and reservoir pressures are close to hydrostatic pressure, around 250 bar. Seawater injection is utilized to increase recovery and for pressure support. With Ba^{2+} levels ranging from 60 to 300 ppm, downhole sulphate scale deposition caused by seawater injection was identified in well A-28 in May 2000.

The reservoir sands are in general poorly consolidated and contain 20–30 % clay minerals, as shown in Table 1. Kaolinite is the dominant clay mineral and occurs commonly as pore fills and coatings, often packed as sub-rounded aggregates with poor crystal face development. Other type of clay minerals is mica and illite, which range from 5 to 10 %. Most of the producing wells have sand control devices installed (gravel pack or stand alone screen). Well productivity is high prior to water breakthrough. However, a rapid decline in productivity is noted after water breakthrough in perforated and gravel packed wells with prepacked sand screens that have been stimulated with mud acid/clay acid treatments. Water related productivity decline in open hole completed wells occurs at significantly higher water cuts.

Downhole scale control presents a particular severe challenge due to a combination of high Ba^{2+} concentration in the produced water, significant fines migration, demand for environmental friendly chemicals, strong top-side emulsion tendency, limited hydrostatics and at times high draw down within the gravel packs. Aqueous and non-aqueous squeeze treatments have been deployed on Heidrun since late 1999 to provide scale control. However, several wells have suffered

productivity loss due to fines plugging in the gravel pack, which is believed to be caused by the overflush fluid volumes used during scale squeeze treatments.

Background

A range of aqueous and non-aqueous scale inhibitor chemistries has historically been deployed to control scale under Heidrun conditions including phosphonates, phosphate ester and various polymer based products. Water based phosphonate and phosphate ester based scale inhibitor treatments whilst delivering acceptable squeeze life have generally led to either formation damage through fines mobilisation, topside emulsion formation and/or are less environmentally acceptable^{1,2,3}. A novel phosphorus containing end-capped polymer was first deployed on Heidrun in January 2002, leading to increased squeeze duration. However, squeeze life was still short and fines mobilisation problems were still common and thus an alternative treatment strategy was required to maximise squeeze life and reduce fines mobilisation.

Under the joint R&D program an environmentally acceptable, multi-functional additive was developed to meet the challenges in extending squeeze life and effecting clay stabilisation on Heidrun. Additives were considered and evaluated for their potential to offer an environmentally acceptable treatment regime that extended scale inhibitor squeeze life. The laboratory procedures adopted to assess the suitability of the candidate additive to extend treatment life are detailed later in this paper. The following section describes the mechanisms believed to be responsible for the effects of the additive on treatments both in the laboratory and in the field.

Inhibitor bridging

Scale inhibitors can be retained in the reservoir by a number of mechanisms including adsorption and precipitation. The retention mechanism will be dictated by the inhibitor type and concentration, brine chemistry including pH, reservoir temperature and rock mineralogy. At lower pH, the weakly acidic scale inhibitor will tend to be more protonated/associated and thus can be retained on the rock surface through hydrogen bonding and Van der Waals forces. At higher pH, the scale inhibitor will tend to more dissociated and thus it can be retained on the rock surface by Van der Waals forces and static electric forces due to metal ion bridging^{6&7}.

The predominantly anionic nature of scale inhibitors presents a less attractive molecule to the traditionally more negatively charged silica surface and thus does not encourage retention. One potential route for increasing inhibitor retention requires the modification of the rock surface to create a more positively charged surface for adsorption and thus a less repulsive

surface to negative charged scale inhibitors. Additives were identified that contained the desired functionality to adsorb onto the more negatively charged rock surface and a suitable isoelectric point to present a more positive charge at low pH values. Such an additive may be expected to adsorb strongly onto the rock surface through hydrogen bonding and Van der Waals force, altering the double layer and thereby the interaction forces between chemicals and the mineral surface. Thus, such an additive should present a less repulsive surface to negative charged scale inhibitors. The pre-treatment of the reservoir zone with the additive or a combination of the squeeze chemical and the additive may therefore be expected to enhance the scale inhibitor adsorption through a bridging type mechanism.

Clay Stabilisation

Nearly all oil producing sandstone contains some clay, occurring as a coating on individual sand grains and/or discrete particles mixed with the sand. The clays most frequently found in hydrocarbon zones are bentonite, illite, kaolinite and chlorite⁸. In the presence of low salinity aqueous fluids bentonite would be expected to swell whilst illite, kaolinite and chlorite may be classed as non-swelling clays.

Clays can be destabilised and thus encouraged to move with the produced fluids when they are exposed to changes in brine salinity and pH, the presence of non-native fluids including chemicals and changes in flow rate. Well interventions introduce foreign liquids including water and chemicals into the formation, which may induce clay instability through the disruption of the forces binding the clay particle and sand. Clay particles can be entrapped in fluids that move at high flow rate. The moving particles can deposit in capillary constrictions/or plug the pore space causing a reduced permeability.

Clays particle migration can be minimised through the careful selection of the carrier brines used for well interventions such as sodium, potassium or ammonium chloride brines, the deployment of selected polymer additives⁹, careful control of fluid pH and the minimisation of injection and production flow rates into and from the well. Selected polymers can coat the rock surface, including the clay particles, causing them to adhere more strongly to one another. This increases the force needed to mobilise the reservoir fines and thus reduces their tendency to be produced.

The authors considered that the selected additive may possess desirable fines stabilising properties. This was noted in carefully designed laboratory sand pack tests and subsequent field experiments that is the subject of other publications^{10,11}.

Experimental

The laboratory test work reported in this paper was performed using the following materials:

Brine:	6% of NaCl brine.
Chemicals:	A = Phosphonate
	B = Phosphate ester
	C = Phosphorus end-capped co-polymer
	D = Maleate polymer
	F = Multi-functional additive

Industry standard test procedures were performed to confirm that the three scale inhibitors were compatible with Heidrun produced brines, were thermally stable and capable of managing the scale risks associated with Heidrun. In addition, the compatibility of the multifunctional additive with Heidrun produced brines and the phosphorus end capped co-polymer was evaluated, its thermal stability was confirmed and its impact on the inhibition performance of the phosphorus end capped co-polymer was determined.

Experimental Procedure of Adsorption (Bridging) Tests

The core materials used in this study were crushed from the core plugs from Heidrun field and sieved to less than 2 mm size fraction. The disintegrated rock material was then allowed to dry before the adsorption tests. The adsorption test procedure can be summarised as follows:

1. Prepare both scale inhibitor and Additive F solutions at 5000 ppm as supplied in 6% NaCl(w/w).
2. Adjust the stock to the required pH values.
3. Weigh out 8 gram of disintegrated rock material and pour into a 60 ml HDPE bottle.
4. Add 16mls of Additive F at given pH and mix with the crushed core. After 4 hours, replace 10 ml of the supernatant with 10 ml of the scale inhibitor solution. After 24 hours, the inhibitor concentrations in the supernatants were then analysed and scale inhibitor adsorption was calculated.
5. This test was repeated in the absence of Additive F using just 6% NaCl brine at the required test pH to condition the crushed core prior to introduction of the scale inhibitor under evaluation.

All tests were performed at 85°C. Blank samples without scale inhibitor and control samples without crushed core were included in the tests.

Phosphonate A, phosphate ester B and co-polymer C were analysed by direct measurement of the phosphorus content via Inductively Coupled Plasma Atomic Emission Spectroscopy

(ICP). Inhibitor D was analysed by a modified version of the Hyamine technique. Additive F was analysed using an in-house developed technique.

Experimental Procedure of Core Flood Tests

Core floods were designed to evaluate the effect of the multifunctional additive on the scale inhibitor return profiles of Inhibitor D. The results from two core floods are presented in this section. Core flood 1 and 2 were performed in the presence and absence of an Additive F pre-flush respectively.

Rock Substrate: The core material was a highly quartzitic "Clashach" outcrop sandstone. The Clashach sandstone material originated from a quarry near Elgin in Scotland. This substrate is often used as an analogue core material for comparative inhibitor adsorption/ desorption core floods.

Brine: Heidrun formation water was adopted. Sulphate ions were omitted for the purposes of this core flood study. The brines were filtered through a 0.45 µm membrane filter prior to use. The brine was adjusted to pH 6.5 prior to injection.

Outline Procedures:

Core flood 1:

- Brine (100% FW) Saturation at room temperature (20°C) following which the temperature was raised to 85°C.
- Brine Permeability and Porosity (Lithium tracer) at 85°C.
- Preflush (i): 5 pore volumes of 6% NaCl injected at 85°C.
- Preflush (ii): 5 pore volumes of 6% NaCl plus 50ppm Lithium injected at 85°C.
- Preflush (iii): 5 pore volumes of pre-flush solution of Additive F injected at 85°C.
- Main treatment: 10 pore volumes (10% as supplied scale inhibitor D plus 50 ppm Li in NaCl) injected at 85°C.
- Shut In, 16 hours at 85°C.
- Inhibitor Release Profile over approx. 1000 pore volumes of post flush with brine (100% FW) at 85°C.

Core Flood 2

In core flood 2 the pre-flush with Additive F was omitted. All other conditions remained identical to core flood

Results

Bridging – Laboratory Data

Scale inhibitor adsorption onto Heidrun crushed core material pre treated with 6% NaCl solution and with 5000 ppm of the multifunctional bridging additive are reported in Table 2. The percentage increase in inhibitor adsorption achieved with the additive is also summarised in Table 2.

The data in Table 2 suggests that:

- The application of Inhibitor A resulted in the highest mass of retained inhibitor on crushed Heidrun core material. Inhibitor C produced the next highest level of adsorption, whilst Inhibitor B produced the lowest level of adsorption.
- The application of all three of the scale inhibitors at low pH (pH 3) generally increased the mass of scale inhibitor retained on the crushed Heidrun core material.
- Pre-treatment of the crushed core material with 5000ppm of Additive F generally increased the mass of all three of the inhibitors retained on the core material when compared to the level of adsorption attained through the pre-treatment with 6% NaCl alone. This was irrespective of the pH of the applied scale inhibitor.

The data indicated that the adsorption of phosphonate, phosphate ester and polymeric scale inhibitors was enhanced through the application of the selected Additive. It is postulated, in the absence of physical and chemical measurements that the adsorption of the Additive F at low pH leads to a less negative rock surface and a less repulsive surface to a negative charged scale inhibitor. Thus the subsequent application of the scale inhibitor to the core material is enhanced through bridging of that inhibitor to the Additive already retained on the rock surface.

Core test data

The inhibitor return profiles for core floods 1 and 2 are presented in Figure 1. The data suggests that the concentration of Inhibitor D in flood 1 in the presence of Additive F fell below 1ppm after 180 pore volumes. In the absence of Additive F the concentration of Inhibitor D fell below 1ppm after the elution of 100 pore volumes. This data reinforced the opinion that the presence of Additive F in the squeeze treatment package would increase squeeze life.

The laboratory derived data was sufficient to convince the Heidrun Asset to deploy the Additive on a trial basis.

Bridging – Field Data

A number of generically different scale inhibitors have been squeezed on Heidrun well A28 as part of the assets strategy to evaluate the potential to extend treatment life and the potential to achieve this using environmentally acceptable chemistry. All treatments were performed using similar treatment designs to allow a representative comparison of squeeze duration.

Early squeezes on this well were undertaken with a phosphonate based scale inhibitor. This was superseded with a polyaspartate based treatment^{1,3} and more recently replaced with the novel phosphorus end capped polymer. In addition

the novel phosphorus end capped polymer was deployed in conjunction with Additive F. The scale inhibitor returns concentration as a function of the produced water volumes from four sequential squeeze treatments using the phosphonate, polyaspartate, phosphorus end capped polymer and the end capped polymer with Additive F are presented for comparison purposes in Figure 2. It should be noted that the minimum inhibitor concentration (MIC) requirements have steadily increased as the seawater fraction in the produced water has increased towards 25%. This has driven the requirement to find more effective scale inhibitors.

The phosphonate deployed in Treatment 1 protected the production of approximately 30,000m³ of brine before the inhibitor return dropped below the laboratory determined minimum inhibitor concentration (MIC) at the seawater fraction present in the well at that time. This was determined to be 10ppm, see Figure 2, Table 3. Treatment 2, performed with polyaspartate, was less effective, protecting the production of just 20,000m³ of brine before the inhibitor return dropped below the laboratory determined MIC at the higher seawater fraction present in the well at that time. This was determined to be 10ppm, see Figure 2, Table 3. Treatment 3 was performed with the novel phosphorus end capped polymer. The application of this inhibitor protected the production of approximately 35,000m³ of brine before the inhibitor return dropped below the MIC at the seawater fraction present in the well at that time. This was determined to be 20ppm, see Figure 2, Table 3. In Treatment 4, Additive F was deployed as part of a pre-treatment to enhance scale inhibitor adsorption and aid fine stabilization. After the pre-treatment stage the phosphorus end capped co-polymer was squeezed. This multi-stage treatment, using the same volume and concentration of scale inhibitor and overflush fluids protected the production of approximately 52,000m³ of brine before the inhibitor return dropped below the MIC determined in the well for the current seawater breakthrough level. This was 24ppm; see Figure 2, Table 3.

To allow the optimization of future treatments on this well and to further understand the effect of the multi-functional additive on inhibitor retention and release properties, Squeeze V¹² was used to simulate the Treatments 3 and 4. The simulation data generated for Treatments 3 and 4 are presented in Figures 3 and 4. As highlighted above, Treatment 3 was performed with the phosphorus end capped polymer whilst Treatment 4 consisted of an Additive F pre-flush followed by a squeeze with the phosphorus end capped polymer.

To match the field returns data from the two treatments with and without Additive F a different set of isotherm parameters was required, see Figures 3 and 4 and Table 4. The Freundlich isotherm was found to give the best match to these two treatments. The Freundlich parameters K and n indicate the inhibitor adsorption property. A larger K and n value indicate higher levels of adsorption of the scale inhibitor onto the rock surface. The Freundlich parameter r₂ defines the inhibitor

adsorption/desorption rate constant. A larger r_2 value indicates a faster rate of inhibitor adsorption/desorption from the rock surface whilst a smaller r_2 indicates a slow rate of inhibitor adsorption/desorption from the rock surface.

The Freundlich parameters identified for Treatment 3 in the absence of the bridging additive were insufficient to describe the return curve obtained from Treatment 4 with the pre-flush additive. A larger K , n and r_2 value than that required to fit Treatment 3 (800, 0.16 and 0.29 respectively) was necessary to match Treatment 4 (1200, 0.4 and 0.11 respectively). This indicates that Additive F alters the rate and extent of inhibitor retention and release. This could only take place if Additive F presented a new surface for the scale inhibitor to adsorb onto.

A new Heidrun well was subsequently treated with the phosphorus end capped polymer in conjunction with Additive F, resulting in the protection of over 90,000 m³ of produced brine, see Figure 5. In these treatments, the multi-functional additive was preflushed before the main scale inhibitor injection. It should be noted that because of the success of the treatments on the initial trial well described above, this new well has not yet been squeezed in the absence of Additive F.

Field Data - Clay Stabilization

The field data presented in this section are from scale squeeze treatments performed on five wells in the Heidrun field. Wells A-28 and A-52 were treated with the multi-functional additive and wells A-48, A-51P, and A-29 were treated with the other scale inhibitors, such as the oil soluble phosphonate and the water based phosphate ester. Figure 6 shows the productivity expressed as the productivity index PI against time for Well A-48.

PI calculation and monitoring at Heidrun has been discussed elsewhere⁴. For a dry oil well producing above bubble point, we calculate the PI as

$$PI_o = \frac{Q_o}{P_R - P_{wf}} \quad (1)$$

Where Q_o is the oil rate, P_R is the reservoir pressure and P_{wf} is the well flowing pressure.

When water breaks through, a common approach is to calculate the so-called liquid productivity index PI_l by replacing Q_o with the total liquid rate ($Q_o + Q_w$) in Eq (1). However, a consistent method for comparing the PI before and after water breakthrough must take into account the difference in flow properties between oil and water. To do that, one approach is to calculate what the oil PI would have been if the well produced no water. If straight line relative permeability curves are assumed, the relation between (dry well) oil PI and liquid PI is:

$$PI_o = \frac{PI_l}{1 + (\alpha - 1)WC} \quad (2)$$

Where WC is the water cut and $\alpha = \mu_o B_o k_{rw} / \mu_w B_w k_{ro}$. For only water flowing ($WC = 1$), Eq. (2) can be reduced to $PI_w = \alpha PI_o$. Also for more realistic relative permeability curves, Eq. (2) is approximately correct if oil and water primarily flow in different zones.

Any loss of PI can imply an oil production decrease. The decrease of PI can be related to a formation damage in the near well bore area, such as plugging of pores and screens by mobilized fines, scale deposition etc.

Figure 6 shows the PI changes for the time period between 25 July 2000 and 20 February 2001 in well A-48. It can be seen that after the scale treatment of 28 October 2000, the PI drops sharply from 35 to 20. After that PI continues decreasing to about 16. In this squeeze treatment, an oil based phosphonate inhibitor was used. Compatibility tests show that the scale inhibitor is compatible with the Heidrun fluids, so clay migration was assumed to be the main cause of formation damage.

Figures 7 and 8 show the PI changes for wells A-51P and A-29. The time period displayed for well A-51P is from 16 October 1998 to 24 January 2000. The time period displayed for well A-29 is from 21 September 1998 to 14 November 2000. Both figures show that after water breakthrough the productivity index decreases rapidly. It was suggested again that clay particle migration might block the gravel pack and the near well bore area. Acid stimulation was designed to remove the clay particles.

The acid treatment was carried out on 8 November 1999 for well A-51P and on 18 April 2000 for well A-29. The stimulation effect of the acid treatments is clearly seen in both Figures 7 and 8. After the acid treatments, the PI increased, indicating a removal of fines and resulting in increased oil production. However, following the acid treatments, scale inhibitor treatments were carried out. After the scale squeeze treatments in well A-51P on 15 November 1999 and in well A-29 on 15 July 2000, the PI immediately decreased, indicating re-plugging of the wells. The water based phosphate ester was used in A-51P, and the oil soluble phosphonate inhibitor was used in A-29.

The effects are different when the treatments are performed in wells A-52 and A-28 with the multi-functional additive. Figure 9 shows PI changes in the period from 15 March 2000 to 5 November 2001 for well A-52. Following an acid wash on 18 July 2000, the scale inhibitor squeeze was performed on 19 July 2000. Unlike the scale treatments in the other wells, the PI recorded in this well did not decrease. Instead, it increased from below 30 to above 30. PI increased even further to above 40 after June 2001. The field data suggested

that Additive F provided a level of clay stabilisation normally noted with more conventional clay stabilising additives. This finding was further supported by the treatments for well A-28.

Figure 10 shows *PI* changes in the period from 5 March 2000 to 28 July 2001 for well A-28. After the scale milling on 26 June 2000, a total of 6 scale inhibitor squeeze treatments were carried out. In all treatments, the multi-functional additive was deployed. Figure 10 shows that even if the *PI* is fluctuating somewhat, the scale squeezes didn't have significant negative impact on *PI*. In other words, the multi-functional additive reduced the clay particle migration.

Technology Value

The deployment of Additive F as part of a pre-flush treatment before the main scale inhibitor pill has resulted in an averaged increase in squeeze treatment life of 50%. This reduced the number of squeeze treatments performed from approximately 18 to 12 per year on well A28. In addition this increased the net availability of the well from 40-50% to 60-70%. This reduces both chemical and operational costs including deferred oil costs. A well that ideally could produce oil at 1000 Sm³/d would increase its annual production by 72500 Sm³ which at the current high oil price is valued at over 90 Million NOK. This is in addition to the chemical savings that have been made in reducing the total number of treatments performed.

In addition the use of Additive F has significantly reduced the need to stimulate other wells with mud and clay acids. This has given further reductions in well intervention frequency, increased net well availability and lowered stimulation costs.

Summary and Conclusions

- The Heidrun field presents a challenging scaling environment because of the high barium content in the formation water, the use of seawater for pressure maintenance and the clay rich sandstone, which generates a significant amount of fines during normal and unplanned operations.
- Aqueous and non-aqueous scale inhibitor treatments have been performed on Heidrun including the use of phosphonates, phosphate esters, polymers and a novel phosphorus end capped co-polymer. In most cases the application of the squeeze treatment has resulted in an increase in the mobilisation of reservoir fines leading to plugging in the gravel packs and thus reduced *PI*.
- A joint R&D programme has identified an additive, which provides enhanced adsorption of the scale inhibitor and an acceptable level of fines stabilisation.

- Laboratory studies have demonstrated that the additive increases the adsorption of a range of different scale inhibitor types on crushed Heidrun core material. In addition it provides more desirable scale inhibitor release characteristics in core flood tests. The tests indicated that the additive provides a certain level of scale inhibition that may complement that provided by the scale inhibitor.
- Field trials have demonstrated that the additive extends the scale inhibitor treatment life and reduces the mobilisation of fines.
- Simulation data generated using Squeeze V indicate that increased *K* and *n* values and a lower *r2* value (Freundlich parameters) were required to match the field treatment using the additive versus the values required to match the treatment performed without the additive. This suggests that more adsorption was taking place but at a slower rate in the presence of the additive.
- The deployment of the additive has resulted in an averaged 50% increase in treatment life with an annualised deferred oil saving of approximately 72500 Sm³ which at current oil prices is valued at over 90 Million NOK on one well alone.

Acknowledgements

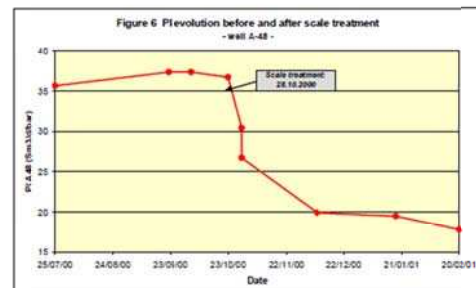
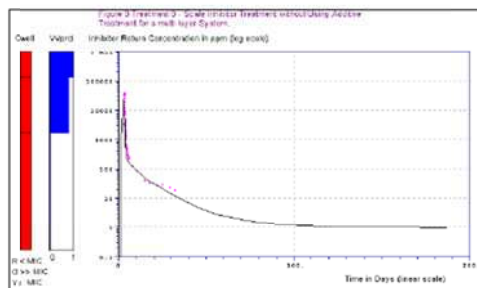
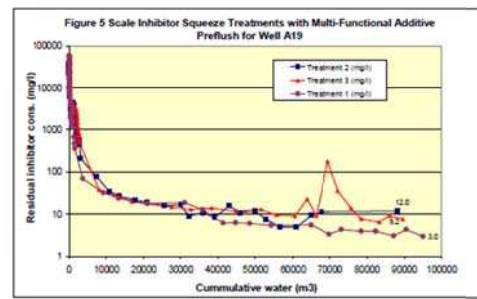
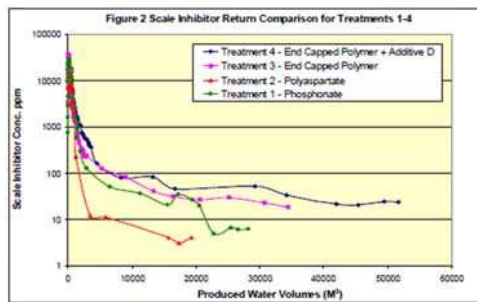
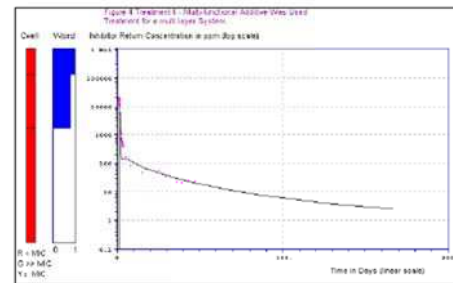
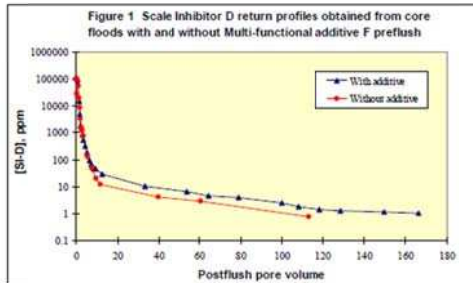
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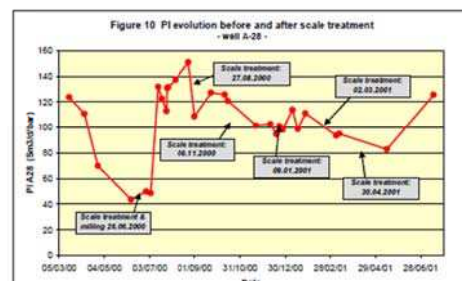
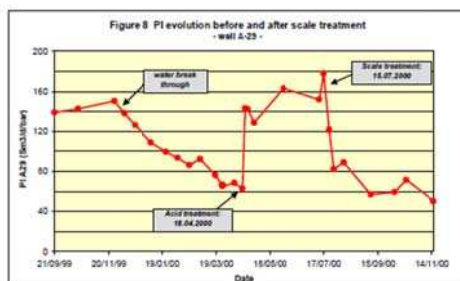
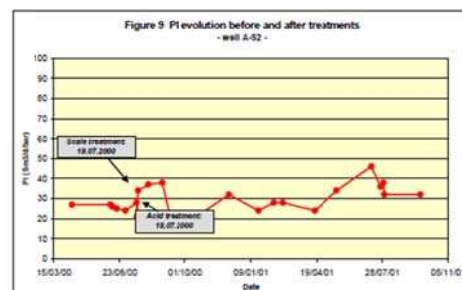
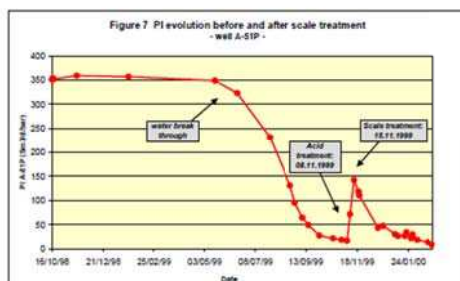


Table 1 Heidrun Mineralogy

Reservoir Zones	Quartz (wt%)	Feldspars (wt%)	Mica/Illite (wt%)	Calcite (wt%)	Siderite (wt%)	Pyrite (wt %)	Kaolinite (wt%)
Garn	52	9.3	3.6	<1	<1	12	26
Ile	53.3	5.1	8.9	<1	1.5	1.8	29
Tilje	39.9	15.3	2.4	<1	9.2	10.6	22.8
Are	49.4	11.1	10.1	<1	1.1	0.2	24.9

Table 2 Enhanced Adsorption of Scale Inhibitors A-C

Sample	Pre-conditioning	Inhibitors	Adsorption mg/g	% increase in adsorption
1	NaCl 6%, pH =3	Inhibitor A at pH 3	4.53	
2	Additive, pH =3	Inhibitor A at pH 3	4.91	8.44
3	NaCl 6%, pH =3	Inhibitor A at pH 5	3.82	
4	Additive, pH =3	Inhibitor A at pH 5	4.04	5.87
5	NaCl 6%, pH =3	Inhibitor B at pH 3	1.68	
6	Additive, pH =3	Inhibitor B at pH 3	1.85	9.87
7	NaCl 6%, pH =3	Inhibitor B at pH 5	1.59	
8	Additive, pH =3	Inhibitor B at pH 5	2.01	26.61
9	NaCl 6%, pH =3	Inhibitor C at pH 3	3.17	
10	Additive, pH =3	Inhibitor C at pH 3	3.19	7.07
11	NaCl 6%, pH =3	Inhibitor C at pH 5	2.87	
12	Additive, pH =3	Inhibitor C at pH 5	3.16	10.09

Table 3 Treatment Life Comparison

Treatment	1	2	3	4
Scale inhibitor	Phosphonate	Polymer	Co-polymer	Co-polymer with additive preflush
MIC ppm	10	10	20	24
Treated Water Volume	30000 m ³	20000 m ³	35000 m ³	52000 m ³

Table 4 Freundlich Parameters Used in Squeeze V Simulations

	Treatment 3	Treatment 4
K	800	1200
n	0.16	0.4
f ₂	0.29	0.11

SPE 80377

A Way Beyond Scale Inhibitors – Extending Scale Inhibitor Squeeze Life Through Bridging

Olav M. Selle, Rex M.S. Wat, Olav Vikane and Haavard Nasvik, Ping Chen, Thomas Hagen, Harry Montgomerie, Hugh Bourne

Peer review by Dr Gordon M. Graham. 25th August 2014

SPE 80377 was published in the proceedings of the 2003 SPE International symposium on oilfield scale. The work focussed on the development of a new technology to improve the lifetime of conventional scale inhibitor squeeze treatments while minimising the potential for formation damage which could result in certain oilfields due to the mobilisation of fine (silica based) material during standard treatments. Like SPE 50706 this paper also described a significant new, and very different, technological advancement based on the research conducted by the authors.

The paper describes clearly the technical challenge being tackled by the researchers; that being the need to conduct downhole scale inhibitor squeeze treatments into poorly consolidated reservoirs which had previously resulted in damage (oil productivity impairment) due to fines mobilisation. The second challenge was to achieve improved (extended) treatment lifetimes.

The paper describes the use of additional (none scale inhibiting) chemicals designed to bind fine clay material in the reservoir therefore preventing damage while at the same time aid the adsorption of the scale inhibitors while also stabilising

The paper describes the mechanisms believed to control the effectiveness of the additive blend at solving both challenges and described results from both laboratory research and field applications (field trials) which confirmed the positive benefits of this treatment strategy. In essence the paper described the use of cationic polymers to enable clay stabilisation which when bound to the reservoir rock surface provided an additional / improved adsorption surface for the anionic scale inhibitors to react and bind – thus was described as “bridging”. This therefore allowed increased retention of the scale inhibitor and subsequently longer treatment lifetimes.

This paper represented the first publication of this technological advance in the oilfield scale community and led to the subsequent publication of several additional papers describing further advances in this technology as well as application papers relating to further field trials. Indeed as recently as May 2014 new papers covering additional research developments of this technology were published in the 2014 International oilfield scale symposium.

In my opinion this paper presented an excellent technical advancement for downhole scale inhibitor squeeze treatments in poorly consolidated fields, resulting in two significant achievements (i) reduction in damage due to stabilisation of fines and (ii) extension in treatment lifetimes due to improved retention of the scale inhibitor via a bridging mechanism between the anionic scale inhibitor and the surface adsorbed cationic additive - a mechanism which is still described in papers published as recently as May 2014 on this topic. The technology presented was new and novel. The paper provided sufficient details of the mechanisms of the research and technological advancement that enabled the reader to understand both the application challenge being faced, the new concept adopted to solve the challenge and also the technical advancements made. I have also referenced the paper in several presentations and also reference it when presenting an SPE (Society of Petroleum Engineers) approved short course on inorganic scaling. In my opinion the paper is high technical quality and worthy of publication on many oil industry peer reviewed journals.

Dr Gordon M. Graham
Managing Director
Scaled Solutions Ltd.

Reviewed: 25th August 2014.



SPE 100466

Field Experiences in the Application of an Inhibitor/Additive Interaction Package to Extend an Inhibitor Squeeze Life

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Abstract

Since the middle 1980s, seawater breakthrough has been observed for a number of wells in a major offshore Field operated by Statoil. This Field has also several tie-ins. Both sulphate and carbonate scale deposition has been identified in the near well bore area and tubing. Inhibitor squeeze treatments were regularly carried out to prevent wells from damages due to scale precipitation. The conventional phosphonate scale inhibitor (DETA-phosphonate) was often used. Some of the sandstone formations in the oil field are relatively "clean" with very little amount of clay materials i.e. Ertve and Tarbert formation. As a result, a relatively short inhibitor squeeze life was seen in these formations after the squeeze treatments with a phosphonate scale inhibitor. Other reservoirs had acceptable squeeze life, but due to environmental requirements a wide set of inhibitors was studied.

In order to reduce the well intervention frequency and extend an inhibitor squeeze life, a method involving a polymer interaction between a polymer scale inhibitor and polymer additive has been developed. In addition to the enhanced adsorption; attributed by the surface charge modification by the adsorption of the positively charged polymer additive on the sandstone surface, the interactions between polymer inhibitor and additive further increase the inhibitor retention in the formation. This polymer interaction approach is different from a conventional precipitation squeeze where calcium chloride was used. Also, unlike the conventional precipitation squeeze, the polymer additive can be pre-injected and rapidly adsorbed onto a rock surface. The subsequently injected inhibitor will react with the additive on the rock surfaces, resulting in a precipitation on a rock surface. This avoids the bulk precipitations where a permeability reduction was often

caused by a conventional precipitation squeeze. During the production, the precipitated polymer inhibitor was released through a hydrolysis process.

This paper presents a detailed method and field results based on the treatments using the polymer inhibitor and additive package in the oil field. The application of polymer interaction package significantly improved the inhibitor squeeze life. Satisfactory results have been achieved from the field trials. The unique polymer reaction package satisfies the stringent Norwegian environmental regulations of low toxicity, high biodegradation and low bioaccumulation.

Introduction

The Field is located in the North Sea, in the northern portion of the Viking Graben and straddles the border between the Norwegian and UK sectors. The Field was discovered in 1973, declared commercial in August 1974, and started production in 1979. The field has been developed with three condeep production platforms. All of them have concrete gravity base structures incorporating storage cells. Production is from the Brent, Dunlin, and Statfjord reservoirs, with the main reserves in the Brent and Statfjord reservoirs.

Two of the satellite fields are involved in the field scale inhibitor squeeze treatments. The satellites are located 17 and 6 kilometers north and east of the main Field. They are tied back to the main Field through sub sea flowlines.

Typical formation brine chemistry is displayed in Table 1. After seawater breakthrough, both sulphate and carbonate scale has been identified in the near well bore areas and tubing.^{1,2,3}

More recently scale build up in the 7" re-entry guide was confirmed during caliper logging in June 2003 in one of the wells. Severe scale build up was detected in the wire line re-entry guide, which prevented access to the formation interval. The scale control strategy for the field has been a combined scale dissolver and scale inhibitor squeeze treatment.

Although the strategy of combining inhibitor squeezes with dissolver treatments was considered acceptable, relatively short squeeze life has been observed in some of the wells that were completed in very clean sandstone formation. Furthermore, the increasingly stringent environmental regulations have highlighted the need to substitute the phosphonate chemistry and traditional DTPA/EDTA based scale dissolvers deployed on the main Field. Efforts were made to study the inhibitor squeeze life extension and to

identify environmentally acceptable squeeze chemicals. As a result, some novel additives for extending scale inhibitor squeeze life and effective environmentally acceptable scale inhibitor chemistry have been identified. Several publications have outlined both experimental and field data as well as treatment methods in the development of "green" chemicals and the additives used to extend the inhibitor squeeze life.^{2,3,4} This paper presents further experimental results, treatment methods and field results based on the field treatments using a polymer inhibitor and additive package.

Literature Review and Theoretical Background

In order to achieve a good inhibitor squeeze lifetime, it is essential to achieve good inhibitor retention without damaging the formation for an inhibitor squeeze treatment. Scale inhibitors can be retained in the reservoir by a number of mechanisms including adsorption and precipitation. For an adsorption squeeze treatment, an inhibitor adsorption level is affected by a number of factors such as inhibitor type and concentration, brine chemistry, pH, reservoir temperature and rock mineralogy. At lower pH, the weakly acidic scale inhibitor will tend to be more protonated / associated and thus can be retained on the rock surface through hydrogen bonding and Van der Waals forces. At higher pH, the scale inhibitor will tend to be more dissociated and thus can be retained on the rock surface by a number of mechanisms including weak Van der Waals forces and electrostatic forces due to metal ion bridging.^{5,6} Tremendous efforts have been made in the research into the new methods in the design of the longer inhibitor squeeze lifetime. In 1992, it was reported that an enhanced inhibitor adsorption could be achieved from a surface binding process due to the presence of calcium ions.⁵ The calcium ions may modify either the electro-chemical properties of the solid surface or they may complex with the inhibitor to aid adsorption. This calcium-enhanced adsorption process has been referred as the surface precipitation.

Apart from the surface charge modification using Ca^{2+} to increase an inhibitor adsorption, Ca^{2+} was often involved in an inhibitor precipitation squeeze treatment to extend the treatment life. It was reported in 1983 and 1987 that in limestone and sandstone reservoirs, the precipitation squeeze involving Ca^{2+} had extended the inhibitor treatment lifetime.^{7,8} In the precipitation squeeze, the Ca^{2+} is thought to react with a scale inhibitor, forming a complex of Ca^{2+} /inhibitor. At an appropriate temperature, pH and concentrations, Ca^{2+} /inhibitor complexes will turn into precipitates, resulting in an increased inhibitor retention hence extending an inhibitor treatment life. A paper published in 1997 showed that the solubility and dissolution rate of Ca^{2+} /inhibitor complex precipitates had a significant influence on the inhibitor return concentration during back production stage of the inhibitor core floods.⁹ In 1999, it was reported that the organic activator additives were formulated with a scale inhibitor/divalent metal ion solution, which allows control of the final solution pH and thus the nature of the inhibitor precipitate formed.¹⁰ The core flood testing in the study further highlighted the potential for extended inhibitor treatment lifetime with no significant losses in permeability to oil or brine.

Instead of involving calcium, a number of methods were introduced in order to extend the inhibitor squeeze treatment lifetime. In 2000, it was reported that the inhibitor retention could be enhanced by the ester cross-linking of polycarboxylic scale inhibitors, leading to an improved inhibitor return curve.¹¹ In 2002, a method using miscible displacement to extend squeeze lifetime was introduced.¹² The method involves an oil-in-water microemulsion-based scale inhibitor formulation which displayed a significant extension in treatment life compared with an aqueous baseline treatment.

Since 2000 efforts have been made to develop a method to extend the inhibitor squeeze life. Several chemical additives have been identified that could be used to provide an effective method to increase the inhibitor retention on the rock surface. The chemical additives are positively charged chemicals and can be rapidly adsorbed onto the negatively charged rock surfaces. As a result, the adsorbed additives present a less negatively charged surface than the rock itself, altering the double layer and thereby the interaction forces between chemicals and the mineral surface with which the scale inhibitor compounds can interact. The inhibitor was expected to be adsorbed on the additive coated rock surfaces through electrostatic forces, hydrogen bonding and Van der Waals force. The pre-treatment of the reservoir zone with the additive or a combination of the squeeze chemical and the additive is therefore expected to enhance the scale inhibitor adsorption through a bridging-type mechanism. Several publications have outlined the experimental results, treatment methods and field data for which an enhanced inhibitor treatment lifetime was achieved.^{3,13,14,15}

It was found that at the given pH, temperature and concentration, the additive reacted with a selected scale inhibitor, forming white gel like precipitates, as shown in Figure 1.⁴ As a result of the reaction, the inhibitor retention levels on the rock surface were significantly higher than that of controlled sample without using the additive. Table 2 summarizes the comparison level of the inhibitor retention onto the rock particles with and without the additive. At pH 3, the presence of the additive almost doubled the amount of the inhibitor adsorbed compared to the adsorption level of the reference sample due to the precipitation reaction. At pH 5, the inhibitor retention level increased by only 30 % compared to the adsorption level of the reference sample. The core flood tests confirmed that the inhibitor/additive interaction also significantly improved the release characteristics of the inhibitor. As shown in Figure 2, the interaction between the additive and inhibitor leads to a better inhibitor return than that without the additive.

Inhibitor/Additive Interaction Package and Field Application Method

It was found that at given pH, temperature, inhibitor and additive concentrations, the specific function group of the additive actually reacted with the polymer inhibitor, forming a gel like precipitate. However, this reaction can be a reversible process. Once the pH, temperature and brine chemistry are changed, the precipitate will dissolve and scale inhibitor will separate from the additive. The reversible process is a hydrolysis process. pH plays an important role in the reaction between the additive and the polymer inhibitor. At low pH,

the reaction occurs towards the formation of precipitates. Higher pH condition is favorable in the hydrolysis process where the precipitate dissolves. The precipitation reactions between the polymer and additive, coupled with the inhibitor adsorption, can significantly increase the inhibitor retention on a rock surface. In addition, the additive also acts as a rock surface charge modifier as mentioned above.

Core flood testing involving the polymer inhibitor/additive interaction package, confirmed good inhibitor return. Thus, it was expected that this process can be used to extend the inhibitor squeeze lifetime.

The study led to a number of field trials in which the additive was preflushed at a concentration normally between 5 to 10%, and followed by a brine spacer. Then, the main pill of scale inhibitor was injected, at 5 to 10% followed by displacing the pill into the formation. The pH of the preflush additive and main pill scale inhibitor solution was carefully controlled before pumping. When the production was resumed after the shut-in, the inhibitor was desorbed when contacted with the produced water. A schematic view of the process is shown in Figure 3.

Experimental Details

Extensive experiment work was performed in order to qualify the chemical additive/polymer inhibitor package. The compatibility beaker and dynamic loop tests were conducted at field conditions. The core flood work was also carried out to study the inhibitor desorption characteristics and a comparison was made to check if an enhanced inhibitor return, was achieved. The experimental results, together with the data from the first field trial, have been reported previously.⁴ In this study, a further core flood using the chemical additive and polymer inhibitor package was conducted. The compatibility and dynamic loop tests at field conditions were also carried out.

The laboratory test work reported in this paper was performed using the following materials:

Brine: 6% of NaCl brine and, formation brine. The brine chemistry is presented in Table 1.

Chemicals: The inhibitor used is phosphorus containing end-capped co-polymer. The additive is a multi-functional agent.

In the test program, the scale inhibitor selected for use in the field was tested using OSPAR Commission guidelines. Testing through independent GLP approved laboratories were performed. The independent GLP tests confirmed that both inhibitor and additive provided satisfactory environmental properties. Both Inhibitor and additive are classified as 'yellow' according to the Norwegian Pollution Control Authority (SFT).

Rock Substrate: The core material used was representative of the formation. The sandstone core plug was from Munin sand in the Draupne formation and its mineralogy analysis is listed in Table 3. It is seen that the core plug is relatively "clean" and mainly consists of quartz with less than 3% of Kaolinite.

Basic Tests: Industry standard test procedures were performed to confirm that the inhibitor was compatible with produced brines and seawater and thermally stable at test conditions. In addition, the compatibility of the additive with produced brines and seawater was evaluated. Its thermal stability was confirmed.

Dynamic Loop Tests: Dynamic scale loop tests were performed to evaluate the performance of the inhibitor at field conditions. The tests were performed at worst-case barium sulphate scaling conditions (50/50 synthetic, formation water and synthetic seawater). The conditions for the dynamic loop tests were:

Temperature:	98°C
pH:	5.5
Flow rate:	10 ml/min.
System Pressure:	100 psi

The test coil was pre-scaled in the absence of scale inhibitor to create a standard test surface. The minimum inhibitor concentration (MIC) was identified as the lowest concentration of scale inhibitor required to prevent an increase in differential pressure of more than 1 psi over a three-hour test period.

Experimental Procedure of Core Flood Tests: The core flood was designed to test the additive/polymer inhibitor package and to evaluate the inhibitor return profiles and a potential formation damage issue. The interaction between the polymer inhibitor and additive was controlled by adjusting the pH of 10% inhibitor solutions. 10% inhibitor solution was made at a pH of ~3 to ensure a precipitation interaction between the polymer inhibitor and the additive. The core flood procedure was outlined as follows:

1. Initial synthetic formation brine injection.
2. Overnight crude saturation and heat up to 98°C.
3. Pre-treatment permeabilities to crude oil in forward flow (FF) and reverse flow (RF) directions, T = 98°C.
4. Pre treatment brine saturation at 98°C.
5. Pre treatment brine permeabilities in FF and RF directions, T = 98°C.
6. Formation water injection in RF direction, at 98°C.
7. Preflush injection (5 pore volumes of 10% Additive in 6% NaCl brine) in RF direction at 98°C.
8. Shut in (5 hours) at 98°C.
9. Main chemical injection (10 pore volumes, 5% Inhibitor in 6% NaCl brine at pH ~3 in RF direction at 98°C.
10. Shut in (overnight) at 98°C.
11. Oil injections and permeabilities to crude oil in forward flow (FF) and reverse flow (RF) directions, T = 98°C.
12. Inhibitor return profile – FF Direction – 5 days at 98°C (100%, FW).
13. Post treatment brine, permeabilities in FF and RF directions, T = 98°C.
14. Post treatment crude saturation at 98°C.
15. Post-treatment crude permeabilities in FF and RF directions, T = 98°C.

Experimental Results

Dynamic Scale Loop Tests: Dynamic scale loop tests were performed to evaluate the performance of the polymer inhibitor at Field conditions. The tests were performed at worst-case barium sulphate scaling conditions (50/50 synthetic formation water and synthetic seawater). The loop test results show that the MIC of the polymer inhibitor was 10ppm.

Inhibitor Return Profile of the Core Floods: The inhibitor effluent profiles during inhibitor post-flush stage of the flood is shown in Figure 4. The core plug was taken from the Munin sand in the Draupne formation. The inhibitor concentration in the core flood was 5%. The preflush additive was used at 10%. As seen from Figure 4, the inhibitor concentration is still over 30 ppm after more than 500 pore volumes of the brine postflush. This gives a comparable result with the previously reported core flood conducted using a Field core plug.³ In this flood the inhibitor concentration was 10% without preflush additive. Comparing the floods with and without preflush additive clearly shows that the core flood with preflush additive gives a better inhibitor return profile than without the preflush additive. In particular, it should be mentioned that the injected inhibitor concentration in the flood using the additive is only half of the flood without using the additive.

Permeability Evaluations of Core Flood: Table 4 shows the determined crude oil permeability recorded at the stages before and after the chemical applications. From Table 4, it can be seen that 93 % of oil permeability was recovered after the injections of both additive and polymer inhibitor. The initial average oil permeability at 98°C was recorded at 970 mD. After the injection of the inhibitor and additive, the flow back average oil permeability was determined at 907mD.

Injection Pressure Profiles: Injection pressure profiles recorded during the additive preflush and main pill inhibitor injections are presented in Figure 5. A stable differential pressure was recorded throughout the pre-flush and main pill inhibitor injection stages. Very low differential pressures (< 0.5 psi) were observed, indicating that neither the pre-flush nor the main chemical injection stages in the core flood caused formation damage.

Field Treatment Results

Based on the laboratory studies, the method to deploy the scale inhibitor using the additive and polymer inhibitor package has been applied. Several field trials were then successfully carried out in the Field. The selected wells had "clean" sand formations. In this paper, the field data and experiences learnt from these selected squeezes, using the additive/inhibitor interaction package are presented in the following sections.

Case 1 – Squeeze Treatment to Well A: This well, had a 7" completion and was perforated. It produced with a water rate of 3300 m³/d. After water breakthrough the well productivity starts to decrease due to scaling. A scale dissolver job was carried out in May 2004. However, after a couple of months, it was seen that the well productivity decreased again. It was then decided to carry out a new scale dissolver treatment to regain some of the lost productivity.

Meanwhile, it was also decided to carry out the inhibitor squeeze treatment following the scale dissolver treatment. In the inhibitor squeeze treatment, the combined additive and inhibitor package was considered to use. In October 2004, the squeeze treatment was conducted using the following design:

Preflush:	10 m ³ 2% KCl
Preflush-2:	60 m ³ 10% Additive in 6% NaCl.
Main pill:	220 m ³ 5% Inhibitor in seawater.
Overflush:	100 m ³ (0.1% inhibitor in seawater)
Shut in:	12 hours

The treatments were performed by bullheading. After the treatment, the well bean up was carried out without any problem. Also, no process problems were reported during the back production. In the treatment, 10 m³ of 2% KCl was injected as a spacer between the produced fluid and the additive. The KCl brine was also used to prevent a potential clay swelling. The additive was deployed as a part of the pre-treatment to enhance scale inhibitor retention through the precipitation interaction. After the pre-treatment stage the inhibitor at 5% in seawater was squeezed. As shown in Figure 6, the treatment for the well has protected more than 200,000 m³ of produced water without loss of well productivity. The ability to protect large volumes of water significantly contributes to economic benefits to the field.

Case 2 – Squeeze Treatment to Well B: A drop in the production index and production was observed in well B following the seawater breakthrough, indicating that scale deposition occurred in the near well-bore area. In January 2005 a scale dissolver treatment was carried out to regain some of the lost productivity. This was followed by a scale inhibitor treatment to prevent further scale deposition. The productivity increased after the first scale dissolver step and it was decided to perform a second dissolver treatment. Then a scale inhibitor treatment was conducted using the additive and inhibitor package.

The squeeze treatment was conducted using the following design:

Preflush:	10 m ³ 2% KCl
Preflush-2:	60 m ³ 10% Additive in 6% NaCl.
Main pill:	220 m ³ 5% Inhibitor in seawater.
Overflush:	200 m ³ (0.1% inhibitor in seawater)
Shut in:	12 hours

The inhibitor return profile and ion data for the treatment are shown in Figures 7 and 8 respectively. Figure 7 shows the treatment for the well has protected approximately, 160,000 m³ of produced water without loss of the well productivity. The ion track data in Figure 8 obtained from the well clearly documents the effect of the combined dissolver and inhibitor treatment. Before the inhibitor squeeze treatment, the barium concentration had dropped to 2 mg/l and increased to above 10 mg/l after the treatment. The barium concentration was kept above 10 mg/l until August 2005.

Case 3 – Squeeze Treatment to Well C: Well C is a satellite subsea template well. Following the seawater breakthrough, the oil production from this well decreased from

500 Sm³/d to 30 Sm³/d. A combined scale dissolver and inhibitor squeeze treatment was performed. The scale dissolver treatment was followed by a scale squeeze treatment with the following design:

Preflush:	10 m ³ 2% KCl
Preflush-2:	60 m ³ 10% Additive in 6% NaCl.
Main pill:	220 m ³ 5% Inhibitor in seawater.
Overflush:	330 m ³ (0.1% inhibitor in seawater)
Shut in:	12 hours

As seen from Table 5, the oil production was quickly recovered from 30 Sm³/d before the treatment to 615 Sm³/d after. The oil rate was kept at 430 Sm³/d for two months after the treatment. At the time of writing the paper, the oil production is still maintained at 420 Sm³/d. The water cut also dropped from 77% before to 53% after the treatment. This treatment has so far protected approximately 65000 m³ of produced water and is still effective.

The squeeze lifetime of the above three well treatments using the additive/polymer scale inhibitor package is summarized in Table 6. The squeeze life of using a phosphonate inhibitor is also presented in Table 6. As shown in Table 6, using additives increased the treatment life significantly. However, it is difficult to compare phosphonate versus polymer inhibitors. Treatment life of scale inhibitor treatments in different wells are difficult to evaluate. Individual differences in well and completion design, reservoir flow characteristics and formation quality may significantly influence the scale inhibitor treatment life.

Conclusions

- At given pH, temperature and concentrations, the selected additive can react with the polymer scale inhibitor. A precipitate forms which increases inhibitor retention.
- Unlike the conventional calcium/inhibitor precipitation squeeze, the additive can be pre-injected and rapidly adsorbed on a rock surface.
- Core flood tests confirmed that the additive/polymer interaction package improved the scale inhibitor return curve. The floods also show no significant permeability reduction.
- The treatment method using the additive and polymer interaction package has been developed. The field results from three field trials demonstrated that the scale inhibitor treatment lifetime could be extended in the application of the package.

Nomenclature

DETA: Diethylenetriaminepenta methylenephosphonate
 EDTA: Ethylenediaminetetra acetic acid
 DTPA: Diethylenetriaminepenta acetic acid
 GLP: Good laboratory practice.
 MIC: Minimum inhibitor concentration.

OSPAR Commission: Oslo Paris Commission.
 SFT: Norwegian Pollution Control Authority.
 SEM: Scanning electron microscopy.

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Table 1 Formation Brine Chemistry

Ion	Conc. mg/l
Na ⁺	8500
Ca ²⁺	400
Mg ²⁺	70
K ⁺	200
Ba ²⁺	60
Sr ²⁺	60
Cl ⁻	13500
HCO ₃ ⁻	1100

Table 2 Inhibitor Retention Level Comparison (Ref. 4)

Pre-Conditioning	Retention mg/g at pH 3	Retention mg/g at pH 5
6% NaCl brine	3.9	3.9
10% Additive at pH 3	7.6	5.0

Table 3 Core Plug Mineralogy Analysis

Quartz % % (w/w)	Kaolinite	Calcite	glauconite
>90	< 3%	trace	trace

Table 4 Permeability Comparison

	Before chemical application	After chemical application & Shut-in
Average Permeability mD	970	907

Table 5 Water and Oil Production before and after the Combined Scale Dissolver and Inhibitor Treatments – Well C

Test Date	Water Cut (%)	Oil Rate sm ³ /day
18.04.05	50	500
22.05.05	58	440
12.07.05	77	30
19.09.05	53	615
21.11.05	56	430

Table 6 Treatment Comparison

Well	Inhibitor package	Volume (m3) and Conc (%)	Treated Brine Volume (m ³)
	Phosphonate	140 (10%)	48,000
A	Additive/polymer inhibitor	220 (10%)	200,000
B	Additive/polymer inhibitor	220 (10%)	160,000
C	Additive/polymer inhibitor	220 (10%)	65,000*

* Well is still producing.

Figure 1 SEM of the precipitates between inhibitor and selected additive (Ref. 4).

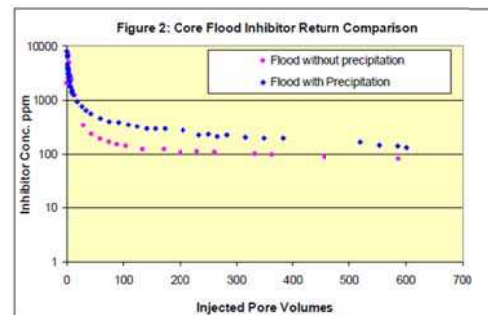
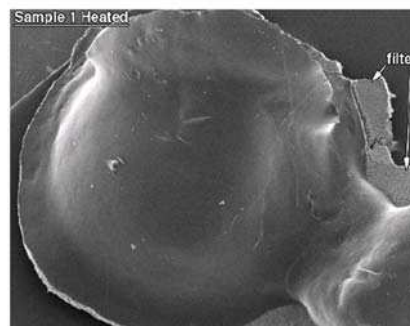


Figure 3 Schematic diagram of the Inhibitor/Additive Interaction /desorption

